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CHEMICAL ENGINEERING SERIES

The Chemical Process Industries

BY

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Professor of Chemical Engineering
Purdue University

FIRST EDITION
FOURTH IMPRESSION

McGRAW-HILL BOOK COMPANY, INC.
NEW YORK LONDON
1945

THE CHEMICAL PROCESS INDUSTRIES

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THE MAPLE PRESS COMPANY, YORK, PA.

This book represents a lifetime of experience in the chemical industry. As such it should be and is dedicated to him who helped to give the author his start in the chemical field—

Edward Mallinckrodt, Jr.

PREFACE

With the increasing recognition of chemical engineering as the basic technology underlying the production processes of many industries, there has developed a need for better understanding of the interrelation of the various fields of application. This is especially true in educational institutions where the student often finds it difficult to bridge the gap between the fundamental theory and engineering, on the one hand, and the practical use of this knowledge in industry, on the other. Although several excellent texts, manuals, even encyclopedias of industrial chemistry are available and find wide use in liberal arts colleges and elsewhere, the modern chemical engineering curriculum calls for closer correlation of industrial procedures with the study of the unit operations and unit processes. In other words, the need is for industrial chemistry presented from the chemical engineering viewpoint. This has been the primary objective sought by the author in preparing this book. Other objectives and the ways in which they have been approached are explained in detail in Chap. I.

The question of nomenclature is often a troublesome one, particularly for industrial usage. It is difficult to get people in industry to employ the scientific nomenclature such as has been adopted by *Chemical Abstracts*. In most cases this text follows the scientific nomenclature of *Chemical Abstracts* with the exception that for long, complicated organic names hyphens are inserted frequently to break these names into their component parts. This is much better than the writing of these names as separate words as is done so frequently in industry. An example is the writing of chloro-nitro-benzene rather than as chloronitrobenzene or as chloro nitro benzene. However, as a concession to wide industrial usage, glycerine is used rather than glycerol and gelatine rather than gelatin.

Meanwhile, many acknowledgments must be made to those who have aided in the preparation of this book. It could not have been written without the helpful cooperation of many experts in the chemical field because the subjects covered are so broad as to be beyond the personal knowledge of any one man. Accordingly, the various chapters have been reviewed, in some instances several times, by chemical engineering authorities actually working in the different fields. Various firms have been cooperative in supplying data for flow sheets and illustrations. Many illustrations are specifically acknowledged at appropriate places.

Over a hundred of the illustrations are flow sheets taken from the recently issued fourth edition of "Chem. & Met.'s Chemical Engineering Flow Sheets," which has been revised and enlarged by T. R. Olive, associate editor of *Chemical & Metallurgical Engineering*, in cooperation with the author of this book. It is the author's opinion that these flow sheets have established a new pattern of excellence for the outline and diagrammatic presentation of chemical engineering processes. Therefore, in many instances, the presentation of different industries and manufacturing operations in this book is closely related to the Chem. & Met. Flow Sheets. Grateful acknowledgment is made to the editors and publishers of *Chemical & Metallurgical Engineering* for making these copyrighted charts available for use in the present volume.

For time and effort spent in reading and criticizing certain chapters in this book, the author is indebted to his colleagues in university work, especially Professors R. H. Ewell, D. B. Keyes, R. F. Newton, P. A. Tetrault, Thomas DeVries, and G. Bryant Bachman. For specific help in collating and abstracting the literature, the author is obligated to J. C. Lottes, Charles H. Prien, Helen Austin, John H. Lux, Lyle W. Rothenberger, Charles J. Marsel, William Resnick, Roy J. Taylor, J. M. Willis, B. L. Moulthrop, and Robert A. Philips. Appreciation is also expressed for assistance in making diagrams and charts to George Austin, R. D. Etherington, T. E. Kline, D. G. Frier, Betty J. Holmes, and A. L. Triesback. Special acknowledgment is due to Helen and George Austin, with Elizabeth Prentiss, for preparing the index.

For assistance on specific chapters, it is a pleasure to thank Eskell Nordell of the Permutit Company, H. B. Rasch of Infilco, R. P. Oliveros of the Semet-Solvay Engineering Corporation, J. H. Pratt of the Liquid Carbonic Corp., W. R. Wood of Girdler Corporation, Charles W. Johnston of the Virginia Smelting Company, Herbert Insley of the Bureau of Standards, A. E. Douglass, Jr., of the Separation Process Company, Henry Chesny, Consulting Chemist, W. A. Gale, American Potash and Chemical Corporation, John W. Turrentine of the American Potash Institute, Inc., Frank J. Tone and W. J. Soley of the Carborundum Company, C. P. Zergiebel and Henry W. Easterwood of the Victor Chemical Works, C. M. Dean and T. R. Harney of Monsanto Chemical Works, C. O. Brown, Consulting Chemical Engineer, Arnold Alt, Mallinckrodt Chemical Works, Jerome Alexander, Consulting Chemist, E. J. Cardarelli, Consulting Chemist, J. W. Bodman of Lever Brothers, A. S. Richardson of Procter and Gamble, E. W. Rice of the National Sugar Refining Co., Arthur C. Lansing of Reichhold Chemicals, Inc., Frank M. Crawford, Paul Bachman, and Arthur W. Campbell of Commercial Solvents Corporation, Mark O. Lamar of the Norton Co., Allen F. Clark and H. A. Lubs of the DuPont Co., H. F. Wiegandt of Standard Oil of Indiana, and J. M. Coahran, Consulting Chemical Engineer, and many others.

R. NORRIS SHREVE.

PURDUE UNIVERSITY,
LAFAYETTE, INDIANA,
February, 1945.

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THE CHEMICAL PROCESS INDUSTRIES

CHAPTER I

OBJECTIVES[1]

Chemical engineering has been well defined for the American Institute of Chemical Engineers as follows:

> Chemical engineering is that branch of engineering concerned with the development and application of manufacturing processes in which chemical or certain physical changes of materials are involved. These processes may usually be resolved into a coordinated series of unit physical operations and unit chemical processes. The work of the chemical engineer is concerned primarily with the design, construction, and operation of equipment and plants in which these unit operations and processes are applied. Chemistry, physics, and mathematics are the underlying sciences of chemical engineering, and economics its guide in practice.[2]

These unit operations or *physical* changes and these unit processes or *chemical* changes may be accepted as the units or blocks into which we can break down the manufacturing processes of the various chemical industries. Many now hold that these two concepts bring unifying principles into what was previously a large, diversified group of apparently unrelated industries. Beginning in Chap. II, this book correlates these two concepts as they are applied to the various chemical process industries.

The objectives sought are to present a cross section of the manufacturing procedures employed by modern chemical industries, largely separated into their unit processes and unit operations through the help of flow charts. The presentation is from the viewpoint of the fundamental chemistry involved in the changes necessary to make the processes operate and of the energy released or absorbed in the reactions, as well as the energy required for evaporation, fusion, and related operations. Because we must have a yardstick to evaluate these industries, domestic statistics[1] of production and consumption are frequently cited with dollar values where available. Likewise costs and other phases of the economic picture are included. Because these are industrial processes, the equipment necessary to carry out the chemical reactions on an industrial scale is of paramount importance.

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[1] This short chapter is actually an introduction to this book, its aims and methods. The author would strongly urge that, when the book is employed as a text, the instructor assign this chapter to the students for study and discussion so that they may early gain a comprehension of the fundamental viewpoints as well as the objectives sought.

[2] NEWMAN, Development of Chemical Engineering Education, *Trans. Am. Inst. Chem. Engrs.*, Supplement to **34**, No. 3*a*, p. 6, July 25, 1938; see also *ibid.*, **32**, 568. (1936).

These chemical process industries not only involve the manufacture of chemicals as such, but they embrace many manufacturing processes based on important chemical changes. Such processes naturally include a considerable variety of operations based on data and principles from other branches of science and engineering. Therefore, it may well be maintained that the chemical process industries represent the summation or the integration of the contributions of many scientists, engineers, and technologists. Specifically, any description of these industries should show the reason why a chemical engineer or an industrial chemist should be interested in inorganic or organic chemistry, physical chemistry, analytical chemistry, physics, mathematics, as well as the modern concept of chemical engineering in its twofold application of unit operations and unit processes. Nor should we forget, of course, that all these activities are carried on to make money and hence exist under the enveloping mantle of sound economics and business principles. Included in this integration should be such other divisions of engineering as strength of materials and the fundamentals of electrical engineering. Hence, to the student, this book may well be the link, or tie, between many of his basic scientific and technical courses, on the one hand, and their industrial application, on the other.

Because of space limitations, very little has been included pertaining to the chemical industries of foreign countries. Their practice is available from the detailed presentation, in many volumes, by Thorpe and Ullmann, to which references are given at the end of this chapter. Nor is any attempt made here to supply the names of companies in the various branches of chemical industry, although there is an occasional reference to a specific company. However, the full listing of such companies is obtainable from a number of trade directories and from the pages of various chemical publications including the "Chemical Engineering Catalog."

Most chemical engineers do not have intimate contact with more than one industry. With this in mind, the text emphasizes not details but broad principles, or a distinguishing characteristic of a certain process or industry. These should be a part of the working knowledge of even the engineer who becomes a specialist, for he never knows when he can translate to his own field a principle that has been put into practice in another process. For the growing number of chemical engineers who enter sales, executive, or management positions, a broader acquaintance with the chemical industry in its entirety is essential. For all these, the specialist, the salesman, and the manager, the flow sheets will present in a connected logical manner an over-all viewpoint of many processes, from raw materials to salable products, such as has been developed so excellently by our competitive system under the economic stimulus and wise temporary protection of our patent laws.

---

[1] **The obtaining of statistics in wartime is handicapped by the rightful withholding of data that would disclose information helpful to our enemies. Hence, many statistics given herein are for the last peacetime year, 1939. In general it may be said that under the stimulus of the Second World War, the chemical output of the United States in 1944 had more than doubled that in 1939.**

The presentation of the chemical process industries around the flow sheets and the energy changes ought to lead to a logical following through of a connected series of unit operations and unit processes, rather than to the memorizing of purely descriptive matter. These will emphasize the *why* rather than the *how* of industrial procedures, or *thinking* rather than *memorizing.*

An engineer has to do with the direction and control of *energy.* This energy may be expended in the moving of molasses in a ship or by rail; it may be employed in the form of heat or steam or electricity, or it may be the energy that is given out in exothermic reactions or that which is absorbed in endothermic chemical reactions. The chemical engineer works with chemical change involving chemical reactions but, on the other hand, in these modern competitive times serious consideration should be given to the other types of energy expenditure connected particularly with the process with which he is concerned. The unit processes consider the change in chemical energy and the resultant effects. Unit operations include the physical changes in energy or position, such as heat flow, liquid flow, or separation; these frequently are an essential part of the fundamental unit process. It is thoroughly believed that the chemical engineer should also consider other broad energy expenditures, such as those represented by the transportation of raw materials. All of these enter into the cost.

The cost of things must be always in the consciousness of the engineer, since he is a part of our industrial system. One of the primary objectives of the engineer's endeavor should be to deliver the best product or the most efficient service at the lowest cost to the consuming public. Therefore, we may well say, quoting from Dean A. A. Potter of Purdue University, "No matter what the numerator may be in an equation one may place before the students in an engineering institution, the dollar sign should appear in the denominator, either apparent or latent."

Every chemical engineer should be familiar with the current selling prices of the principal chemicals with which he is concerned. There is no use in publishing such a list in a book of this nature; these costs change too much and too frequently. To be of any value, such quotations must be secured when the chemical engineer is interested in them. They can be readily had from such journals as the *Oil, Paint and Drug Reporter*, *Chemical and Engineering News*, and *Chemical & Metallurgical Engineering*. Indeed, a corollary to the obtaining of a list of current market prices is the introduction of the chemical engineer to these essential periodicals.

Although this book is not a study in cost determination, there are included many data on the basis of which a cost estimate can be made. Particularly in the flow sheets and in a few other selected parts of the book, approximate figures are given leading to at least the material cost of the product considered, or to labor and material (the so-called *L. & M.*) costs. On the other hand, it is impossible adequately to present or understand the determination of costs without long experience in a particular industry, and too much emphasis cannot be placed upon the inadequacy of the labor and material costs without there being added the various so-called overhead costs, such as research and development expense, depreciation and obsolescence of plant and process, provision for taxes and insurance, and interest on invested capital. These overhead and fixed items often equal or exceed the direct labor and material charges. The cost of chemicals tends to drop as processes are perfected and as production rises.[1]

This book contains no separate chapters on equipment. Specialized books on the subject are available. It was thought better to emphasize equipment in conjunction with the description of the various processes and with the flow sheets representing those processes. On the other hand, any chemical engineer should start early to familiarize himself with industrial equipment such as pumps, filter presses, nitrators, and sulfonators.

The "Chemical Engineering Catalog"[2] includes the most available and convenient information concerning the actual equipment that can be supplied by various manufacturers. In short, it is a yearly résumé of the different catalogs put out by these suppliers. It should be employed as the current apparatus supplement. When this book is used as a text, it is suggested that the instructor so conduct his course that, from time to time, the students are required to go through this catalog and select

[1] ANON., Price Trends, *Chem. & Met. Eng.*, **44**, 553–555 (1937). Besides typical curves of prices or production, this article includes a "10 year price trend for thirty basic chemicals." The annual February issues of this same journal should be consulted for price trends and comments.

[2] Reinhold Publishing Corporation, New York. Distributed annually to *practicing* chemical engineers.

therefrom the various pumps or filter presses or reactors that would be most suitable for the process or flow sheet being studied.

Every chemical engineer, whether in training or in practice, should have as his constant companion the current edition of Perry's "Chemical Engineers' Handbook."[1] Not only are its voluminous tables of data essential to the chemical engineer but also the descriptions and illustrations of apparatus present more about these tools than are contained in any other one volume. The collection of formulas with illustrations is also unexcelled elsewhere. Finally, each section starts with well-selected references for anyone desiring even more details. Because of the excellence of this handbook, particularly covering equipment, many specific references are given to it here when otherwise fuller presentation would have been necessary.

Because of the very considerable number of flow sheets included and the desire to conserve space, not many pictures or line drawings to illustrate the process industries are included in this text. On the other hand, as visual presentation of equipment is extremely helpful, it is advised that instructors, to supplement this text, gather appropriate photographs of plants and equipment from the industries being studied. Quite frequently pictures can be obtained of plants which the students have visited or are planning to visit on their inspection trips. By having all these pictures on lantern slides, they can be used in the appropriate places and in much greater number than would be possible in these pages.

The texts and advertising pages of such journals as *Industrial and Engineering Chemistry*, *Chemical & Metallurgical Engineering*, *Chemical and Engineering News*, together with the very many specialized journals such as *Modern Plastics*, *Sugar*, *Petroleum Refiner*, and many others, should be consulted by the chemical engineer for up-to-date information on equipment and fundamental data.

Usually a chapter is assigned to a given process industry like glass, paper, rubber, or sulfuric acid. Such a chapter has its contents arranged in somewhat the following order:

> After a brief introduction, aimed to epitomize the industry, some aspect is given of the historical side or background of the particular process. This is followed by a consideration of Uses and Economics, including statistical tabulations by which the importance of the industry can be judged. It is well recognized that trends in production, whether on the increase or decrease, are found of more importance than the mere statement that so many pounds or so many dollars' worth of a given substance are being manufactured. This is shown by parallel columns for different years and by statistic curves. Under Manufacture,

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[1] PERRY, JOHN H., editor-in-chief, with a staff of specialists, "Chemical Engineers' Handbook," 2d ed., McGraw-Hill Book Company, Inc., New York, 1941, 3,029 pages of tabulated data and epitomized information. Hereafter this book will be referred to as "Perry, *op. cit.*"

this being a book on chemical engineering, *energy change*, *unit operations*, and *unit processes* are particularly brought to the attention of the reader. For some of the important processes, the principal unit operations and unit processes are tabulated. Dividing the industries into these units helps greatly in the transference of information from one industry to another. Indeed, flow sheets do this same thing in a visual manner. It is felt that by this breakdown the reader will gain a clearer comprehension that filtration or evaporation or hydrogenation or nitration is employed in a considerable number of industries. The source of the *raw materials* and their relationship to the manufacturing procedures are discussed in their economic and chemical relationship. The product of one industry is frequently the raw material of another—indeed, it has been remarked frequently that the chemical industry is its own best customer.[1] Ultimately chemicals stem from the minerals as shown in Table 1 (see also Fig. 1 in Chap. XXXIX). The actual *manufacturing procedures*, in the case of the principal industries, are woven in and around the various flow sheets. Here the raw materials entering into unit operations and unit processes, carried on in industrial equipment, are all connected together. This is the heart of each industry and, although the flow

TABLE 1.—ULTIMATE GEOLOGIC RAW MATERIALS FOR 150 IMPORTANT INDUSTRIAL CHEMICALS[a,b]

	Index number[c]		Index number[c]
1. Water	99	18. Iron ores	6
2. Air	96	19. Phosphate rock	6
3. Coal	91	20. Sea water	5
4. Sulfur	88	21. Copper ores	4
5. Mineral salt	75	22. Fluorine minerals	4
6. Limestone	63	23. Arsenic minerals	3
7. Sulfide ores	32	24. Magnesium minerals	3
8. Brines	24	25. Mercury ores	3
9. Petroleum	23	26. Zinc ores	3
10. Natural gas	16	27. Antimony minerals	2
11. Saltpeter	13	28. Barium minerals	2
12. Potassium minerals	11	29. Boron minerals	2
13. Gypsum	10	30. Manganese ores	2
14. Lead ores	9	31. Tin ores	2
15. Sand	9	32. Bismuth minerals	1
16. Aluminum minerals	8	33. Silver ores	1
17. Chromium ores	7	34. Titanium ores	1

[a] KELLER and QUIRKE, *Ind. Eng. Chem.*, *News Ed.*, **17**, 444 (1939).

[b] Note that coal, petroleum, and natural gas combined equal 130; sulfur and sulfide ores combined equal 120; and salt, brines, and sea water combined equal 104.

[c] Index numbers indicate relative frequency in use. The names of the 150 chemicals are tabulated in the reference.

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[1] *Chem. & Met. Eng.*, **44**, 577–584 (1937); STINE, Relation of Chemicals to Other Industry, *Ind. Eng. Chem.*, **25**, 487 (1933); Charts.

sheets show the general sequence of operations and processes, the text supplements this and refers to the literature for further details.

The order of chapters was determined very largely from a teaching viewpoint. When this book is used in college, the student will frequently be taking physical chemistry and organic chemistry simultaneously. Very largely because of this, it was thought wise to place first those chapters which would be easiest for the student to learn. Hence, such a chapter as that presenting sulfuric acid, involving applications of equilibriums and certain other phases of physical chemistry, is placed after the more purely descriptive chapters pertaining to water, fuels, distillation of coal, gases, and carbon. The sequence of presentation as used in this book has been employed in the classes at Purdue University for a number of years, with an increased ease of learning on the part of students. This seems much better than starting at the beginning of the junior year with a chapter on sulfuric acid and trying to get the student to comprehend the physical and chemical reasons for some of the procedures that have been applied industrially in the manufacture of this important acid. If an instructor wishes to vary the order of the chapters, it will be very simple for him to make a mimeographed sheet, giving the sequence he desires his students to use.

As the aim of a book such as this is to impress upon the reader the quantitative engineering aspects and to lead him to think from raw materials to salable products, the working of problems[1] is of great importance. They also disclose whether the reader has sufficiently mastered the given industry to make calculations concerning its procedures. Therefore, at the ends of the chapters there are a few typical problems pertaining to the industry concerned. However, when this volume is used as a college text, each instructor should supplement these problems with some of his own devising which, for obvious reasons, should be changed from year to year. Since problems at the end of a prospective chapter are the so-called *simple* ones, it would be very helpful if each instructor toward the end of the course would devise comprehensive problems to be given to his class, involving one or more industries, such as are given out each year by the American Institute of Chemical Engineers.[2] In certain universities such comprehensive problems are included in a special problem course. Too much emphasis cannot be placed upon quantitative thinking whether in the practice of chemical engineering or in the living of life in general.

The objectives sought in this volume may be summarized by stating that it has been the endeavor to present the various chemical processes in a generalized form through the correlation into flow sheets and descriptive text of the following:[1]

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[1] PERRY, *op. cit.*, pp. 715–769; HOUGEN and WATSON, "Chemical Process Principles," Part 1, Material and Energy Balances, John Wiley & Sons, Inc., New York, 1943.

[2] Student Contest Problems, *Trans. Am. Inst. Chem. Engrs.*

1. Unit processes: chemical change.
2. Unit operations: physical change.
3. Physical chemistry: equilibriums and reaction rates.
4. Economics: costs, statistics, and consumption.
5. Energy and power: chemical as well as electrical and mechanical.

Selected References

General

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PERRY, JOHN H., editor-in-chief, "Chemical Engineers' Handbook," 2d ed., McGraw-Hill Book Company, Inc., New York, 1941.

Costs and Economics

FURNAS, *op. cit.*, pp. 27–30, for excellent classified bibliography of various phases of chemical economics.

PERRY, *op. cit.*, pp. 2841–2872, with other references on p. 2842.

[1] It is recognized that the limitations of one volume have restricted the full application of all these factors to every process. However, frequent references from text as well as in the Selected References at the end of each chapter will serve to supplement what has been given. The author will welcome suggestions and criticisms of what has been chosen as well as regarding what should be added.

CHAPTER II

UNIT PROCESSES AND UNIT OPERATIONS

In an inexact but expressive manner we may define chemical engineering in its modern sense by the following equation:

$$\text{Chemical engineering} = \underset{\text{(chemical changes)}}{\text{unit processes}} + \underset{\text{(physical changes)}}{\text{unit operations}}$$

The unit process is a very useful concept for technical chemical change and has been described[1] as "*the commercialization of a chemical reaction under such conditions as to be economically profitable.* This naturally includes the machinery needed and the economics involved, as well as the physical and chemical phases." The unit operation is a physical change connected with the industrial handling of chemicals or allied materials; it frequently is tied in with the unit process as when heat flows into an endothermic chemical reaction or out of an exothermic reaction. The unit operation may also be distinctly separated from the chemical change as when, by "flow of fluid," a liquid is moved from one part of an industrial establishment to another.

Chemical engineering, if successfully practiced, requires that the respective unit processes and operations be applied to the various manufacturing procedures. The study of the unit operations on the one hand and of the unit processes on the other is the characteristic of the present stage of this branch of engineering. Indeed, the development of chemical manufacturing procedures is largely through flow sheets which are definitely constructed from a coordinated sequence of unit processes and operations that fabricate the raw materials into the finished product and by-products. In the actual technical application, both unit processes and unit operations are carried on either simultaneously or independently in suitable equipment under the guidance of skilled labor supervised by chemical engineers.

These unit processes and unit operations are the common bond between otherwise widely divergent chemical manufacturing procedures. They, of course, are applied differently under the necessarily varying conditions. Although we hope that we shall have formulas that will enable the chemical engineer to *calculate* at his desk what is going to *happen* in the factory, this millennium has not arrived. There are many

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[1] SHREVE, Unit Processes, Background and Objects, *Ind. Eng. Chem.*, **32**, 145 (1940).

more formulations for the unit operations than for the unit processes, as the latter are more complicated and have only lately been receiving the attention of chemical engineers. Indeed, broad experience is still necessary to apply wisely and economically the formulas and knowledge that are available. In the words of the eminent chemical engineer, W. L. Badger,[1]

> . . . the engineer is the man who must build equipment, assemble it into a process, and make it run, whether or not he has all the theoretical data necessary for its calculation. He must think of equipment in terms not of strictly solved differential equations but of actual chunks of cast iron and steel that somebody shall be able to fabricate, assemble, and operate in terms of a working, practical, economical process.

The characteristics of unit processes as applied to the manufacture of chemicals may be summarized as follows:

1. Each unit process points out the *unitary* or like aspects in a group of numerous individual reactions. This unitary aspect apart from the basic chemical family, may be a similarity in energy change or corrosion or pressure or reaction time or equilibrium or raw materials.

Table 1.—Principal Unit Processes and Unit Operations

Unit Processes	Unit Operations
1. Combustion	1. Fluid flow
2. Oxidation	2. Heat transfer
3. Neutralization	3. Evaporation
4. Silicate formation	4. Humidification and dehumidification
5. Causticization	5. Gas absorption
6. Electrolysis	6. Solvent extraction
7. Double decomposition	7. Adsorption
8. Calcination	8. Distillation and sublimation
9. Nitration	9. Drying
10. Esterification	10. Mixing
11. Reduction	11. Classification
12. Ammonolysis	12. Sedimentation and decantation
13. Halogenation	13. Filtration
14. Sulfonation	14. Screening
15. Hydrolysis	15. Crystallization
16. Hydrogenation	16. Centrifugation
17. Alkylation	17. Disintegration
18. Friedel-Crafts	18. Materials handling
19. Condensation	
20. Polymerization	
21. Diazotization and coupling	
22. Fermentation	
23. Pyrolysis	
24. Aromatization	
25. Isomerization	

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[1] **Badger**, Education, Experience and Engineers, *Ind. Eng. Chem.*, **33**, 1103 (1941).

2. Frequently there is a *factory segregation* by unit processes wherein a building or section of a building may be devoted to the making of many chemicals under a given unit process as diazotization and coupling or nitration or hydrogenation or esterification or fermentation or alkylation.

3. There frequently is a close relationship in the *equipment* used for making many examples under a unit process. For instance, the cast-iron well-agitated reactor, provided with cooling coils, called a *nitrator*, is used for conducting the nitration unit process in the manufacture of a number of chemicals such as nitro-benzene, nitro-naphthalene, or T.N.T.

4. Equipment may be conveniently transferred from the making of one chemical to that of another within the same unit process. It is the aim of a chemical superintendent to keep all his equipment constantly in use. To do this he frequently must make first one chemical then another in the same general reactor—a sulfonator for example. This *multiple use of equipment* is most easily realized under the unit process arrangement.

5. The unit process classification enables a chemical engineer to think from group performance to that of a new individual chemical in the like class. He needs chiefly to remember *principles* rather than specific performances. This method of approach greatly facilitates the making of any chemical by having available past knowledge regarding the generalized data of this unit process. This procedure saves much memorizing of individual observations.

6. As the basis of unit process classification is a chemical one, this places stress upon the *chemical reaction.* Here, usually a slight increase in the chemical yield will materially affect the profit of the manufacturing sequence. Hence the unit process conception lays emphasis upon the necessity for an exhaustive study of the basic chemical change. The cost of raw materials[1] looms up in the cost distribution, being from 50 to 87 per cent of the manufacturing expense. Following the obtaining of the highest possible chemical yield or, if time is available, simultaneously with this study, should go the careful investigation of every unit operation involved, with the aim of saving power or heat or any other physical factor.

7. The *inorganic and the organic procedures* need not be set apart industrially. This, of course, involves no criticism of the traditional separation as a teaching aid. As the equipment and the manufacturing problems are frequently so similar in both organic and inorganic chemicals, it is industrially important to group them together. "The principles[2] involved in the physical chemistry of the basic reactions or the construction and control of the equipment or the economics involved are the same whether organic or inorganic products are obtained." For example,

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[1] SHREVE, *op. cit.*

[2] SHREVE, Inorganic Aspects of Unit Processes, *Ind. Eng. Chem.*, **36**, 411 (1944).

TABLE 2.—UNIT PROCESSES WITH EQUIPMENT

Unit process	Chapter number and industry or product	Equipment
1. Combustion (completed oxidation)	V. Fuel and power	Boilers (steel, firebrick)
2. Oxidation	IV. Water and wastes	Tanks (concrete)
	VII. Water gas	Generators (steel, brick)
	VIII. Industrial gases (CO_2, H_2)	Boilers (steel, brick), reactors (alloy steel)
	XVIII. Phosphoric acid (from P)	Oxidizers (steel and brick)
	XIX. Sulfuric acid	Sulfur burners (steel), converters (steel, cast iron), chambers (lead lined)
	XX. Nitric acid (from NH_3)	Oxidizers (steel)
	XXIV. Paints and pigments	Reactors, kettles, mixers (steel)
	XXIV. Linoleum	Oxidizing rooms (brick)
	XXVII. Perfumes	Reactors (enamel steel)
	XXXI. Fermentation: acetic, citric, and gluconic acids	Tanks (wood), trays (aluminum)
	XXXVIII. Phthalic anhydride	Reactors (steel)
	XXXIX. Formaldehyde	Oxidizers (steel), catalyst (silver gauze)
	XXXIX. Acetic acid (from CH_3CHO)	Reactors and condensers (stainless steel)
	XXXIX. Camphor	Reactors (stainless steel)
3. Neutralization	IV. Water treatment	Treaters (steel), settlers (steel or concrete), reservoirs (concrete)
	XIII. Ammoniated superphosphate	Reactors and bins (steel, concrete)
	XIV. Sodium salts	Kettles, crystallizers (mostly steel)
	XVIII. Na and NH_4 phosphates	Reactors (mostly steel) (lead lined)
	VII. Ammonium sulfate	Absorbers (heavy lead)
	XX. Ammonium nitrate	Absorbers (ceramic lined)
	XX. Urea	Reactors (silver-lined steel)
	XXI. Aluminum sulfate	Tanks (lead lined)
	XXVI. Arsenites, arsenates	Tanks (wood)
	XXIX. Soap from fatty acids	Tanks (stainless steel or Monel)

TABLE 2.—UNIT PROCESSES WITH EQUIPMENT.—(*Continued*)

Unit process	Chapter number and industry or product	Equipment
4. Silicate formation	X. Ceramics	Molds (steel), kilns (ceramic brick)
	X. Sand-lime bricks	Presses (steel), retorts (steel)
	XI. Cement	Kilns (mostly steel, kilns brick lined)
	XII. Glass	Glass furnaces (ceramic blocks)
5. Causticization	XV. Caustic soda	Causticizers (steel)
6. Electrolysis	VIII. Industrial gases (H_2, O_2)	Electrolytic cells (steel)
	XV. Caustic soda and chlorine	Electrolytic cells (concrete and steel)
	XVI. Aluminum	Electrolytic cells (steel)
	XVI. Magnesium	Electrolytic cells (steel)
	XVI. Sodium	Electrolytic cells (steel and brick)
7. Double decomposition	IV. Water softening	Tanks (steel), settlers (concrete)
	XI. Ca and Mg salts	Tanks (steel and concrete)
	XIII. Potassium salts	Reactors (steel)
	XIV. Sodium salts	Reactors (steel, etc.)
	XV. Soda ash	Brine treaters (wood tanks), absorbers (cast iron)
	XVIII. Phosphoric acid	Reactors (lead lined)
	XVIII. Superphosphate	Mixers and bins (iron and concrete)
	XXI. Hydrochloric	Stills (cast iron), condensers (earthenware, tantalum, or carbon)
	XXI. Hydrofluoric	Stills (cast iron), condensers (lead)
	XXIV. Pigments	Reactors (steel)
8. Calcination	XI. Lime	Kilns (rotary, brick-lined steel, or upright of steel and brick)
	XI. Gypsum	Driers (steel)
	XV. Soda ash	Calciners, rotary (steel)
9. Nitration	XXII. Explosives	Nitrators (cast iron or stainless steel)

TABLE 2.—UNIT PROCESSES WITH EQUIPMENT—(*Continued*)

Unit process	Chapter, number, and industry or product	Equipment
	XXXVIII. Intermediates for dyes, nitro-benzene, etc.	Nitrators (cast iron or stainless steel)
	XXXIX. Nitro-paraffins	Nitrators and separating columns, continuous (stainless steel)
	XXVII. Perfumes	Reactors (copper)
10. Esterification	XXXIV. Rayon: xanthate or viscose	Steeping press, shredders, agers, barratte (steel)
	XXXIV. Rayon: acetate	Mixers, acetylators (aluminum)
	XXXIX. Ethyl and vinyl acetate	Reactors (copper or stainless steel)
11. Reduction	XVIII. Phosphorus	Furnaces (steel, brick)
	XIX. Sulfur from SO_2	Reactors (steel)
	XXXVIII. Aniline from nitrobenzene	Reducers (cast iron or wood)
	XXXVIII. *p*-Phenylenediamine	Reducers (cast iron)
12. Amination by ammonolysis	XXXVIII. Aniline from chloro benzene	Autoclaves (steel)
	XXXVIII. β-Naphthylamine	Autoclaves (steel)
	XXXIX. Ethanolamines	Autoclaves (steel)
13. Halogenation	XXII. Chemicals for warfare	Reactors (steel)
	XXVI. Insecticides	Reactors (steel or ceramic)
	XXXVIII. Intermediates for dyes	Reactors (steel or earthenware)
	XXXVIII. Chloro-benzene	Halogenators (steel)
	XXXIX. Benzyl chloride, carbon tetrachloride	Chlorinators (ceramic), reactors (lead lined)
14. Sulfonation	XXII. Explosives	Sulfonators (cast iron or steel)
	XXXIII. Sulfite paper	Burners, sulfite towers, digesters, beaters (mostly steel with towers concrete)
	XXXVIII. Intermediates for dyes	Sulfonators (cast iron or steel)
	XXXVIII. Benzene-sulfonate for phenol	Sulfonators (cast iron or steel)

TABLE 2.—UNIT PROCESSES WITH EQUIPMENT.—(*Continued*)

Unit process	Chapter number and industry or product	Equipment
15. Hydration and hydrolysis (saponification) (alkali fusion)	XI. Slaked lime	Hydrators (steel)
	XVIII. Phosphoric acid from phosphorus pentoxide	Hydrators (ceramic lining)
	XIX. Sulfuric acid from sulfur trioxide	Absorbers (steel tower), cooler coils (steel)
	XXV. Gelatine and glue	Extractors (steel), special driers
	XXIX Glycerine	Soap kettles (steel with top stainless), evaporators and stills (steel)
	XXIX. Soap	Soap kettles (steel with Monel or stainless-steel top)
	XXX. Corn sugar	Acid-resistant low-pressure autoclaves (copper)
	XXX. Dextrin	Same as for corn sugar
	XXXI. Sucrose to glucose and fructose	Fermenters (wood tanks or steel)
	XXXII. Hydrolysis of wood	Acid-resistant low-pressure autoclaves (copper)
	XXXVIII. Phenol	Fusion pots (cast iron)
	XXXIX. Acetaldehyde from acetylene	Reactors (Duriron)
	XXXIX. Alcohols from chlorides and sulfates	Hydrolyzers (steel or lead lined)
16. Hydrogenation and hydrogenolysis	XX. Ammonia from nitrogen	Catalyst chambers (Cr alloy)
	XXI. Hydrochloric acid from chlorine	Reactors (steel), absorbers (earthenware, tantalum, or carbon)
	XXVIII. Hydrogenated oils and fats	Hydrogenators (steel), catalyst (nickel)
	XXIX. Detergents (Hymolal class)	Hydrogenating autoclaves (stainless steel lined)
	XXXVII. Petroleum industry	Catalyst chambers (steel or Cr alloy)
	XXXIX. Methanol from CO	Compressors, heat exchanger, catalyst chambers (steel or Cr alloy)
17. Alkylation	XXIII. Photography	Autoclaves (steel)
	XXXVII. Petroleum industry	Alkylators (steel), bubble towers (steel)

TABLE 2.—UNIT PROCESSES WITH EQUIPMENT.—(*Continued*)

Unit process	Chapter number and industry or product	Equipment
	XXXVIII. Intermediates	Reactors (steel), stills (copper)
	XXXVIII. Dimethyl-aniline	Autoclaves (steel)
	XXXIX. Medicinals	Autoclaves (copper)
	XXXIX. Tetraethyl lead	Reactors (steel)
18. Friedel-Crafts	XXXVIII. Benzoyl-benzoic acid for anthraquinone	Reactors (steel or enamel)
	XXXVI. Ethyl-benzene (styrene)	Reactors (steel)
19. Condensation	XXIV. Resinification	Reactors (steel, nickel, stainless steel)
	XXXIX. Phenolphthalein	Reactors (steel)
20. Polymerization	XXXVI. Rubber	Polymerizers (steel)
	XXXVII. Petroleum industry	Polymerization reactors (steel)
21. Diazotization and coupling	XXXVIII. Dyes	Vats (wood), filters (wood or cast iron)
22. Fermentation	VIII. Industrial gases (CO_2)	Fermenters (wood or steel)
	XXXI. Alcohol and CO_2 from monosaccharides	Fermenters (wood or steel tanks)
	XXXI. Alcohol, acetone, and butanol from carbohydrates	Fermenters (steel tanks)
	XXXI. Wines, beers, and liquors	Fermenters (steel, wood, concrete)
	XXXI. Lactic acid	Fermenters (wood tanks)
	XXXI. Penicillin	Fermenters (steel tanks)
23. Pyrolysis or cracking (thermal decomposition)	VI. Distillation of coal	Retorts (steel-braced firebrick with steel and cast-iron connections)
	VII. Fuel (coal) gases	Retorts (steel-braced firebrick)
	VII. Oil gas for carbureted water gas	Carburetors (brick-lined steel)
	IX. Carbon black	Channel coolers (steel)
	IX. Lampblack	Distillation chambers (steel, brick)
	XXXII. Distillation of wood	Retorts (steel)
	XXXVII. Petroleum industry	Reaction chambers (steel)

TABLE 2.—UNIT PROCESSES WITH EQUIPMENT.—(*Continued*)

Unit process	Chapter number and industry or product	Equipment
24. Aromatization	XXXVII. Petroleum industry	Reaction chambers (steel)
25. Isomerization	XXXVII. Petroleum industry	Isomerizers (steel)
26. Miscellaneous (base exchange) (allotropic change)	IV. Water	Tanks (steel)
	IX. Graphite	Electrothermal furnaces (steel and brick)
	XVII. Calcium carbide	Electrothermal furnaces (steel protected by charge)
	XVII. Silicon carbide	Electrothermal furnaces (steel protected by charge)
	XVII. Carbon disulfide	Electrothermal furnaces (steel and brick)
	XXIII. Photographic industry	Tanks and special equipment (nickel, silver, ceramics, rubber)
	XXV. Leather	Tanks (wood)

there is surprisingly little differentiation in the conditions or equipment used to hydrogenate nitrogen to ammonia, or carbon monoxide to methanol, except in raw materials charged and catalyst employed.

8. The *design* of equipment is greatly aided by the generalizations arising from the unit process arrangement rather than by considering each reaction separately. What experience has indicated for a number of reactions allied under a unit process is an excellent guide for a new reaction in this same grouping.

In handling unit processes, the more that is understood about the underlying physical chemistry of the equilibriums and the reaction rates, the better will be the control, the higher the conversion, and the lower the costs. It is very important to know how fast a reaction will go and how far. Many times, as is pointed out in connection with the manufacture of sulfuric acid by the oleum process (page 377), conditions that increase the rate decrease the equilibrium. Therefore, as is shown in the design of the sulfur trioxide converter, conditions are first secured to cause a high rate of reaction and then, toward the end, are changed to favor the equilibrium. The work that Hougen[1] and others are doing in studying reaction rates is of the utmost significance. It is to be hoped that more chemical engineers and physical chemists will direct their

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[1] HOUGEN, *et al*, Industrial Reaction Rates, Symposium, 10 papers, *Ind. Eng. Chem.*, **35**, 502–580, 677–700 (1943).

TABLE 3.—UNIT OPERATIONS WITH EQUIPMENT

Unit operation	Chapter number and industry or product	Equipment
1. Fluid flow	IV. Water and wastes	Pumps (steel), tanks (steel, concrete)
	XXVIII. Oils and fats	Pumps (steel)
	XXXVII. Petroleum industry	Pumps (steel)
2. Heat transfer	V. Fuels and power	Boilers and heat exchangers (steel)
	VI. Distillation of coal	By-product ovens and regenerators (fire brick)
	VII. Fuel gases	Generators (steel and brick), exchangers and coolers (steel)
	VIII. Industrial gases	Exchangers and liquefiers (steel)
	X. Ceramics	Kilns (steel and firebrick)
	XI. Cement	Rotary kilns (steel, firebrick)
	XII. Glass	Furnaces and regenerators (ceramic blocks and bricks)
	XV. Soda ash	Calciners (steel)
	XVIII. Phosphorus	Electrothermal or blast furnaces (steel, brick)
	XIX. Sulfuric acid	Burners and converters (steel)
	XX. Ammonia	Converters and exchangers (steel)
	XXXVII. Petroleum industry	Pipe furnaces, exchangers, condensers (steel)
3. Evaporation	XIII. Potassium salts	Multiple evaporators (cast iron)
	XIV. Salt	Multiple evaporators (cast iron)
	XV. Caustic soda	Multiple evaporators (nickel lined)
	XVIII. Phosphoric acid	Evaporators (lead lined)
	XXIX. Glycerine	Multiple evaporators (steel)
	XXX. Sugar	Multiple evaporators (steel)
4. Humidification and dehumidification	XXXIV. Textile fibers	Factories (brick, concrete, wood)

TABLE 3—UNIT OPERATIONS WITH EQUIPMENT.—(*Continued*)

Unit operation	Chapter number and industry or product	Equipment
5. Gas absorption	VI. Distillation of coal	Absorbing towers (steel)
	VII. Fuel gases	Absorbers or purifying towers (steel)
	VIII. Industrial gases	Absorbing towers (steel)
	XV. Bleach	Shelves or rotary (concrete)
	XX. Nitric acid	Absorbers and oxidizers (Cr-steel)
	XXI. Hydrochloric acid	Absorbers (ceramic, tantalum, or carbon)
	XXV. Leather	Vats (wood)
6 Solvent extraction	VII. Coal gas	Towers (steel)
	XXVI. Insecticides	Percolators (steel)
	XXVII. Perfumes	Percolators (steel)
	XXVIII. Oils	Extractors (steel)
	XXXII. Acetic acid	Extractors (copper or stainless steel)
	XXXII. Rosin	Extractors (copper or stainless steel)
	XXXVII. Lubricating oils	Extractors (steel)
7. Adsorption	IV. Water and wastes purification	Tanks (concrete) for carbon
	XXIV. Artificial leather solvent recovery	Tanks (steel) for carbon
8. Distillation and sublimation	VI. Distillation coal	By-product ovens (firebrick), stills (steel)
	VIII. Industrial gases (O_2, N_2)	Rectifiers for liquid air (steel)
	XXVII. Perfumes	Stills (copper)
	XXIX. Glycerine	Vacuum stills (steel)
	XXXI. Alcohol, acetone	Stills (copper)
	XXXVII. Petroleum industry	Bubble towers, stills (steel)
	XXXVIII. Intermediates	Stills (cast iron, steel)
9. Drying	X. Ceramics	Driers (steel or brick)
	XIV. Sodium salts	Rotary and pan driers (Monel, steel)
	XXIV. Pigments	Box driers (steel)
	XXIX. Soap	Drying rooms (brick and wood)
	XXX. Sugar	Rotary driers (steel)
	XXXIII. Pulp and paper	Steam-heated cylinders (steel)
	XXXVI. Rubber	Driers (steel)

TABLE 3.—UNIT OPERATIONS WITH EQUIPMENT.—(*Continued*)

Unit operation	Chapter number and industry or product	Equipment
10. Mixing	XIX. Fertilizers	Mixers (steel)
	XXII. Dynamite	Mixers (wood)
	XXIV. Paints, lacquers	Mixers (steel)
	XXXVIII. Dyes	Mixing vats (wood)
11. Classification	XI. Cement rock	Beneficiation equipment (steel)
	XVIII. Phosphate rock	Beneficiation equipment (steel)
12. Sedimentation and decantation	XIII. Potassium salts	Thickeners (steel)
	XV. Caustic soda	Thickeners (steel)
13. Filtration	X. Ceramics	Plate and frame filters (iron)
	XI. Ca and Mg salts	Filters (iron and brass)
	XIII. Potassium salts	Filters (iron)
	XIV. Sodium salts	Filters (iron and wood)
	XXX. Sugar	Filters (iron)
	XXXIV. Rayon	Filters before fiber formation (brass)
	XXXVII. Paraffin	Filters (iron)
	XXXVIII. Intermediates and dyes	Plate and frame filters (iron, wood)
	XXXIX. Organic chemicals	Plate and frame filters (iron, wood)
14. Screening	XI. Cement	Screens (iron)
	XV. Soda ash	Screens (iron and wood)
	XVII. Silicon carbide	Screens (iron and wood)
	XXX. Sugar	Screens (iron and wood)
15. Crystallization	XI. Ca and Mg salts	Tanks (steel)
	XIII. Potassium salts	Vacuum and open crystallizers (steel)
	XIV, XVIII. Sodium salts	Crystallizers (steel)
	XXX. Sugar	Crystallizers (steel)
16. Centrifugation	VI. NH_4 sulfate	Centrifuges (copper and iron)
	XI. Ca and Mg salts	Centrifuges (copper and iron)
	XIII. Potassium salts	Centrifuges (copper and iron)
	XIV. Sodium salts	Centrifuges (copper and iron)

TABLE 3.—UNIT OPERATIONS WITH EQUIPMENT.—(*Continued*)

Unit operation	Chapter number and industry or product	Equipment
	XXX. Sugars	Centrifuges (copper and iron)
17. Disintegration	X. Ceramics	Mills (steel)
	XI. Cement	Mills, many types (steel)
	XII. Glass raw materials	Mills (steel)
	XII. Rock wool	Fiber making (steel and brick)
	XXIV. Paints	Ball, cylinder, and disk mills (steel, stone)
	XXXV. Resins	Mills (steel)
18. Materials handling	V. Fuels	Conveyers (rubber, canvas)
	VII. Fuel gases	Pumps and pipes (steel)
	X. Ceramics	Screws, conveyers (steel, rubber)
	XI. Cement	Conveyers (steel, rubber)
	XII. Glass	Special conveyers (steel)
	XV. Soda ash	Screw conveyers (steel)
	XXXII. Wood	Trucks (steel)
	XXXVI. Rubber	Trucks, conveyers (steel)

NOTE. Table 3 is intended to point out only important or striking applications of the unit operation. Indeed it would be difficult to find a chemical industry in which are not used such important unit operations as fluid flow, heat transfer, drying, mixing, and filtration.

attention to the fundamental facts of the reaction rates and reaction equilibriums. All of this will aid in making the unit process conception more quantitative and bring into the unit process field more equations for calculating results.

The unit operations have been given very intensive and fruitful study by most of the college research laboratories in the field of chemical engineering. Since 1915 when Arthur D. Little called particular attention to the importance of these physical aspects and laid the foundation for the modern conception of chemical engineering, these principles have been so well presented by William H. Walker and his coworkers, Lewis, McAdams, and Gilliland[1] together with Badger and McCabe[2] that anyone desiring an understanding of the principles connected with unit operations need only refer to the writings by these authors and many others.

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[1] WALKER, LEWIS, MCADAMS, and GILLILAND, "Principles of Chemical Engineering," 3d ed., McGraw-Hill Book Company, Inc., New York, 1937.

[2] BADGER and MCCABE, "Elements of Chemical Engineering," 2d ed., McGraw-Hill Book Company, Inc., New York, 1936.

Throughout this book, attention is constantly called to unit processes and unit operations since the numerous flow charts are broken down into a coordinated sequence of these units. However, at least a naming of both the principal unit processes and the principal unit operations is in order here and is given in Table 1. The unit processes are the basis of the classification of the various intermediates presented in Chap. XXXVIII and of the miscellaneous organic chemicals included in Chap. XXXIX. Under each unit process in these chapters is included much of a general nature pertaining to that particular unit process. In Table 2 is arranged a listing of the principal unit processes occurring in the various industries together with the main equipment as used in the different fields of the chemical process industries. Likewise, Table 3 presents this same aspect for unit operations.

Selected References

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CHAPTER III

GENERAL FUNDAMENTALS

To carry out commercially the *unit processes* and the *unit operations* in any chemical plant presupposes factory-scale equipment. To keep the factory itself from corroding away, proper materials of construction should have been selected by the designing chemical engineer. To regulate properly the chemical processes requires instruments for recording and controlling the procedures. To avoid harmful impurities in the raw materials, to follow the course of the chemical reactions, and to secure the requisite purity of products require careful chemical control by periodic analyses. To transmit goods in a clean and economical manner from the manufacturer to the customer, suitable containers must be provided. To effect the safety of the workman and the plant, all these procedures must be carried on in a nonhazardous manner. To secure the processes from unfair competition and to ensure an adequate return for the large sums spent on research, the chemical steps and the equipment in the factory must be protected for the limited period granted by the American patent laws. To guarantee progress, to continue profits, and to replace obsolescent processes and equipment, much attention and money must be spent upon appropriate research. To prevent contamination of streams and interference with the rights of neighbors, factories must avoid the discharge of waste materials either into the air or into the streams of their locality.

MATERIALS OF CONSTRUCTION

In chemical factories the successful consummation of chemical reactions and the maintenance of equipment depend not so much upon the strength of the materials as upon their proper selection to resist corrosion and withstand the effects of elevated temperatures and pressures. Mechanical failures are seldom experienced unless there has been a previous corroding or a weakening by chemical attack on the material used for the construction of either the equipment or the building. Thus corrosion is a constant and continuing problem with the chemical engineer in industry.

In some cases corrosion cannot be prevented; it can only be minimized. In these instances the designing engineer must provide for periodic replacements. Fortunately, however, particularly in the past 25 years, the advance of chemical engineering has provided many corrosion-resisting materials. Among such relatively new materials are the following: rubber-covered steel, resin-bonded carbon, and tantalum—all to resist hydrochloric acid—stainless steel to resist the action of aqueous nitric acid even under pressure, and nickel or nickel-clad steel to resist caustic solutions, hot or cold.

Among construction materials used by chemical engineers are to be found many of the commonest products as well as some of the rarest—brick iron, cement, and wood on the one hand and platinum, tantalum, and silver on the other. To choose the proper material, namely, one that will have the strength necessary and the chemical resistance needed, requires that the chemical engineer have an accurate knowledge of the chemical processes for which the materials of construction are needed. He must also know the corrosion resistance of the materials he thinks will be employed. Frequently actual testing will be in order. When any corrosion tests are made, they should not be carried out with pure laboratory chemicals but with the commercial grades not only of the chemicals to be used in the factory but also of the actual construction material to be tested. It frequently happens that a small amount of contaminant in a commercial raw material affects the corrosion very appreciably. An example of this is the attack upon aluminum by dilute nitric acid made from Chile saltpeter which carries a small quantity of halogen.

In recent years many data have been collected and added to the literature pertaining to corrosion, particularly about the properties of the structural materials employed in our chemical factories. For classified specific information reference should be made especially to the books by Speller[1] and Perry.[2] Also the current issues of our engineering journals should be consulted, especially the pages of *Chemical & Metallurgical Engineering*[3] and *Industrial and Engineering Chemistry*.[4] Where metals are concerned, stress corrosion and corrosion fatigue[5] may become very important in high-pressure vessels that are subject to vibration.

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[1] SPELLER, "Corrosion: Causes and Prevention," 2d ed., McGraw-Hill Book Company, Inc., New York, 1936.

[2] PERRY, *op. cit.*, pp. 2091–2166. Here Lee and Calcott lay down directions for conducting corrosion tests. Many excellent tables of properties are given for recommended materials of construction for various uses.

[3] *Chemical & Metallurgical Engineering* has published extensive tables on the properties and materials of construction and corrosion. Many of these tables are reprinted in Perry, *op. cit.*, or have been published as separate pamphlets.

[4] For example, ROETHELI and FORREST, Materials Used in Chemical Engineering Operations, *Ind. Eng. Chem.*, **24,** 1018 (1932); HARCOURT, Designing Efficient Equipment, *Ind. Eng. Chem.*, **33,** 1112 (1941).

[5] MOORE and KOMMERS, "Fatigue of Metals," McGraw-Hill Book Company, Inc., New York, 1927.

The following pages present a general outline of some of the chief materials of construction and their applications to the chemical industries:

Ferrous Materials.—*Steel* is still our main structural material. It is the metal almost universally employed in the construction of most buildings and in the reinforcing of concrete. It is widely used in pipes, tanks, reaction vessels, pumps, valves, and other tools of the chemical process industries.

Under certain conditions its corrosion resistance is excellent, as, for example, in the handling of cool, concentrated sulfuric acid[1] or of mixed nitric and sulfuric acids containing not more than 25 per cent of water. In general, however, practically all dilute acids, even moisture of the air, will cause serious corrosion of unprotected steel surfaces.

Steel is employed extensively, together with cast and wrought iron, for handling dilute alkaline solutions or the neutral organic liquids met in the petroleum and coal-tar industries. When the concentration of alkalies is high or the temperature is raised, there is often some attack upon the ferrous metals, in which case a more costly material such as nickel, Monel metal, or even silver is substituted.

Wrought iron has behind it a long history of service in the chemical industries. Presumably its inclusions of chemically resistant slag provide an increased measure of protection against many corrosives. Wrought-iron pipe is often used in applications where steel or cast iron proves unsatisfactory.

Cast iron resists sulfuric acid and alkali a little better than does steel. Also, when it does corrode, this takes place much more slowly and evenly. Consequently, cast-iron pipe or vessels are preferable when their enhanced weight and greater brittleness do not prevent their use.

High-silicon irons, such as Duriron and Corrosiron containing 14 per cent of Si, are very resistant materials for use with nitric acid, even in low concentrations. They are also preferred for boiling nitric acid. The high-silicon irons cannot be forged or welded, and their castings are somewhat more brittle than ordinary cast iron.

The *stainless steels*[2] consist essentially of iron, chromium, and nickel, with minor but important other constituents. A typical formula is "18:8," containing 18 per cent chromium and 8 per cent nickel. Stainless steels, now among the most important of the construction materials used by the chemical engineer, can be fabricated and welded like other steels, can be forged or cast, and they resist organic acids and nitric acid of all concentrations.

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[1] For details of corrosion resistance of various materials against different strength acids, see Furnas, "Rogers' Manual of Industrial Chemistry," 6th ed., pp. 243, 308–311, D. Van Nostrand Company, Inc., New York, 1942.

[2] SANDS, Stainless Steel Developments in Process Industries, *Chem. & Met. Eng.*, **49**, No. 4, 88–91; No. 5, 132–135 (1942).

Nonferrous Metals and Alloys.— *Copper* for many decades has been a stand-by of the chemical engineer in multitudinous applications. It is relatively inexpensive and can be fabricated into complicated shapes and possesses fair strength. Its chemical resistance against ordinary atmospheric moisture and oxygen is excellent as there is formed an adherent protective coating usually of copper oxide. Copper resists alkali (except ammonia) better than does steel. It resists organic acids except in high concentrations. It should not be used, however, where any mercury will touch it because of the amalgams that are formed. Even a broken mercury thermometer in a copper vessel may give trouble. In the factory it is employed extensively as the material for the construction of kettles, stills, heat exchangers, tanks, and many reactors. It should not be used in contact with ammonia or amines. Copper alloys such as brass, bronze, and admiralty metals are often superior in corrosion resistance and possess better mechanical properties than the pure metal.

Aluminum is applicable to specialized situations where its lightness and relative ease of fabrication are advantageous. Chemically, it resists strong organic acids, nitric acid, and nitrates providing halogens are absent. Corrosion resistance of aluminum is due to the formation of an *adherent* film of hydrated aluminum oxide; the removal of this film by halogen acids or alkalies exposes the metal to what may be rapid corrosion. As in the case of copper, a wide range of special alloys is available for the chemical engineer's use.

Nickel is widely employed for its excellent resistance to alkalies including ammonia. In the manufacture of iron-free caustic soda, nickel or nickel-clad steel is chosen for tanks, evaporator tubes, evaporator bodies, and even for tank cars. Nickel and its alloys also possess very superior mechanical properties. Most widely used of these is *Monel metal* which is a natural alloy of nickel (67 per cent) and copper (30 per cent). Monel is especially important in the food industries.

Lead is another old stand-by in the chemical industries. Its use is particularly advantageous because of its resistance against dilute sulfuric acid. It is almost universally used in the building of chamber plants for the making of sulfuric acid and for the lining of tanks for storage of dilute sulfuric acid. Its disadvantage is its lack of mechanical strength and its tendency to creep. Different lead sections are joined together by what is called *lead burning,* a reducing flame (hydrogen) being used for this purpose.

Silver,[1] particularly in its pure form, has excellent chemical resistance against alkalies and against many organic acids, particularly when hot.

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[1] BUTTS and GIACOBBE, Silver Offers Resistance to Many Chemicals, *Chem. & Met. Eng.*, **48,** No. 12, 76–79 (1941); ADDICKS, "Silver in Industry," extensive bibliography, Reinhold Publishing Corporation, New York, 1940.

Consequently in the preparation of the purest grade of alkali, silver is the metal used. The autoclaves for the manufacture of urea from carbon dioxide and ammonia are lined with silver. This metal is likewise used for the handling of acetic acid. The disadvantage of silver lies in its mechanical weakness. Consequently it is employed whenever possible as a liner to protect metals mechanically stronger.

Tantalum has high resistance against hydrochloric acid and has consequently been used in such specialized equipment as immersion heaters and condensers designed for heat transfer involving hydrochloric acid solutions.

Platinum has long been employed in the chemical industry. At present its application is most essential as one of the catalysts for the contact sulfuric acid process and in the Ostwald ammonia oxidation procedure. In the latter application, to lessen volatilization loss, the platinum is alloyed with 10 per cent rhodium.

Inorganic Materials Other Than Metals.—*Glass* continues the main material used in chemical laboratories. In recent years, glass fabricators, particularly of the Pyrex variety, have been supplying glass pipe and equipment in larger sizes so that glass can be used in specialized applications in chemical factories. Its resistance against thermal shock and almost everything except hydrofluoric acid, strong alkalies, and mechanical stress is very satisfactory. A new glass containing more than 95 per cent of silica is now available. It possesses greatly enhanced resistance against thermal shock (Chap. XII). Glass- or enamel-lined steel vessels, pipes, and tanks are supplied with excellent chemical resistance, particularly to acids such as hydrochloric. Frequently, enameled ware is the only economically satisfactory material for hot hydrochloric acid, particularly for large sizes where the cost of tantalum would be prohibitive.

Silica equipment in a great variety of shapes has long been available and is used for particular applications where bad thermal shock is encountered. Silica is also hard and greatly resists erosion. It is, however, attacked by alkalies, is easily broken, and is expensive.

Ceramic materials, such as chemical stoneware and porcelain, are available for vessels, pipes, and valves of medium capacity and have been employed where acid conditions prevail. Even large tanks are made out of ceramic bricks[1] or tile held together by acid-resisting cements.[2]

Concrete is cheap, easily fabricated, and widely employed where nonacid conditions prevail. Even where mild acid conditions occur, concrete can be protected by various integrating compounds, such as oleic soaps, and by being coated on the outside with special asphalt paints. The difficulty is often to secure a completely homogeneous coating of the asphalt. By going over the asphalt coating with an electric iron, a much more uniform coating can be secured as the air bubbles are "ironed out."

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[1] KINGSBURY, Ceramic Linings for Chemical Equipment, *Ind. Eng. Chem.*, **29**, 402 (1937).

[2] PERRY, *op. cit.*, pp. 954, 2151–2153.

Carbon is very resistant chemically. With the advent of acid-resisting resins, various shapes of carbon products held together by these resins are now on the market. Phenol-formaldehyde resin is one that seems quite suitable for the binding. These carbon[1] materials are supplied in the form of various bricks and building blocks as well as piping, valves, and fittings. Much of the construction material used in some of the modern hydrochloric acid plants is one of these carbon-resin materials sold under the name of Karbate.

Organic Materials of Construction.—*Wood*,[2] by virtue of its cheapness and ease of working, is widely used for equipment handling, neutral solutions, or even occasionally for weak acids such as dilute acetic acid. Wood also resists saline solutions, such as sodium chloride. Consequently wooden tanks, filter presses, and pipes have long been important factors in the construction of our chemical plants. Other materials such as cotton cloth are used as filter media in filter presses. This is particularly advantageous when a neutral or a weakly alkaline solution is being handled. For the filtration of strong alkali, a cloth made out of Monel metal is very satisfactory. For dilute acid filtrations, wool cloth is commonly used and, more recently, Vinylite, one of the newer plastics.

Rubber is assuming increasing importance as a material of construction for the chemical engineer as different varieties are manufactured and made available at reasonable costs. Natural rubber as a liner for steel tanks and pipes has greatly facilitated the handling of hydrochloric acid. Indeed, this acid is now shipped in rubber-lined tank cars. Several of the new synthetic rubbers possess resistance against nonaqueous solvents such as the various products of the petroleum industry. Consequently they have found wide acceptance for the lining of hose to transport these solvents, and also as gasket materials.

Some of the *plastics*[3] are sufficiently resistant to be very important materials for the chemical industries. For instance, a phenol-formaldehyde resin, using as a filler acid-washed asbestos (Haveg), has been fabricated into tanks, pipes, and similar equipment to withstand acids, particularly dilute nonoxidizing acids.

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[1] See Chap. IX, Industrial Carbon, where Karbate materials are described and pictured.

[2] PERRY, *op. cit.*, pp. 2164–2166.

[3] Chapter XXXV; PERRY, *op. cit.*, p. 2160; SASSO, "Plastics for Industrial Use," section on plastics as engineering materials, McGraw-Hill Book Company, Inc., New York, 1942.

PROCESS INSTRUMENTATION

At one time labor was plentiful and chemical operations were carried out on a small scale in individual batches. The skilled chemical engineer now finds that very many of his manufacturing projects, particularly those operated on a large scale, proceed much more economically as *continuous* processes rather than as small-batch operations. These continuous processes have been and can be controlled by the workman, but they give much more uniform results if, after the best conditions are ascertained, these conditions are maintained throughout by the use of modern instruments for automatic control. The chemical engineer should not choose instruments simply to record temperatures or pressures but as reliable tools to control and maintain desired operating conditions. In these large-scale continuous operations. the function of the workman and the supervising chemical engineer is largely to maintain the plant in its proper running order. Under this maintenance, instruments play a very important part.

When chemical manufacturing is on a small scale or when it is not adaptable to continuous procedures, the *batch sequence* should be used. This requires more supervision on the part of the workman and the chemical engineer because usually the conditions of procedure differ from the start through to the finish. Even with this changing picture, instruments give a record which can be compared from batch to batch and which leads frequently to the choice of superior operating conditions.

Instrumentation[1] *for the indicating, recording, and control of process variables is an almost universal outstanding characteristic of modern chemical manufacture.* Instrumentation has been forced to this position of eminence by the increase of continuous procedures, by the increase in the cost of labor and supervision, by the decrease in the cost of capital, by the increase in the scale of chemical procedures, and by the standardization of chemical procedures under *unit operations* and *unit processes.*

Instruments are available that furnish a wide variety of data and controls, such as,

1. *Instantaneous data* from mercury thermometers for temperature, ordinary scales for weighing, and pressure gages for pressure.
2. *Continuous records* from special instruments for recording temperature, pressure, weight, viscosity, flow of fluids, percentage of carbon dioxide, and many

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[1] Rhodes, "Industrial Instruments for Measurement and Control," McGraw-Hill Book Company, Inc., New York, 1941; Perry, *op. cit.*, pp. 2009–2089, contains an up-to-date presentation of the principles and details of instrumentation; Furnas, *op. cit.*, Chap. 5 on Industrial Instrumentation.

other physical and chemical data. In such cases clocks frequently move a chart so that various readings are correlated with time. Recording of electrical energy,[1] required frequently indicates a certain state in carrying out a chemical procedure when a change ought to be made, as in "beating" pulp in a Jordan or crystallizing sugar in a vacuum pan.

3. *Automatic control* of different variables through special instruments for maintaining a desired pressure or temperature or flow [illegible]. These are more or less complicated devices. The simple thermostat used in almost every home as a necessary adjunct to a modern furnace, is a sample of a very simple controlling instrument. This division of instrumentation is a specialty in itself.[2]

CHEMICAL CONTROL

Chemical control has a threefold function in factory procedures: (1) analysis of incoming raw materials, (2) analysis of reaction products during manufacturing, *i.e.*, so-called "process control," and (3) analysis of the outgoing finished products.

The first of these functions is so well established in so many industries as to need but little elaboration here. The chemical manufacturer should not only know the character of the raw materials he is buying but should often set up strict quality specifications to assure the minimum or complete absence of certain undesirable impurities. For instance, the presence of arsenic in the acid employed would be deleterious for hydrolyzing starch to dextrose for food purposes although of lesser significance if the hydrolysis were to produce dextrin adhesives. Well over 90 per cent of the raw materials of the chemical process industries are probably purchased on the basis of chemical analysis.

Process control, the second of our functions, is an essential part of practically all manufacturing operations involving chemical change. Otherwise the reactions may occasionally get out of hand with resulting losses of time and materials. To avoid this, many "in-process tests" should be made at various steps during the progress of manufacturing. This does not mean that an extensive laboratory should be provided in connection with every unit process or operation. Frequently the plant chemist in the control laboratory can devise fairly simple tests to indicate the progress of a given reaction, and these are sufficiently simple and reliable so that the nonchemical workman can be taught to carry them out. If chemical changes are at all complicated, check samples should be drawn and submitted to the control laboratory for a more careful analysis than is possible by the workman in the factory. For proper operation of a plant, close cooperation between the manufacturing and control divisions is essential. They should, however, be independent of each other to the extent that the laboratory results are not subject to the influence of the man in charge of production.

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[1] SHREVE, Graphic Instruments in Chemical Processes, *Ind. Eng. Chem.*, **26**, 1021 (1934).

[2] PETERS, Getting the Most from Automatic Control, *Ind. Eng. Chem.*, **33**, 1095 (1941).

Finally, to ensure that the customer gets material which meets his specifications and which does not vary beyond predetermined limits, a rather complete analysis should be made of the finished product. Most customers, if their purchases represent any considerable sum of money, maintain a laboratory for checking the purity of what they purchase. In case of any dispute between the seller and the purchaser, this is usually settled by referee analysis on the part of some well-recognized and accepted public analyst.

It is interesting to see the increasing importance of physical means for control of chemical procedures. Such instruments as refractometers, spectrophotometers, and photographing apparatus are now being used, often in the hands of specialists, to supplement the old readings of hydrometers and thermometers.

There is no use spending time and money in the careful making of an analysis unless the *sampling* has been adequate. Too often the drawing of the sample is left to an untrained boy, and a highly skilled chemist will spend hours upon the analysis of the sample brought to him. As much thought, care, and supervision should be placed upon the taking of a truly representative sample as is expended upon the chemical work in the laboratory.

Sampling is a specific application of the unit operation of size separation and is so presented by Perry[1] where directions with diagrammatic representation of accepted operations are given in detail. Basic factors in sampling are summarized in the following paragraphs by Thomas A. Wright:[2]

> No analysis, no matter how adequately performed, can be better than the sample. A sample must be representative of either the material per se or that part or parts which require analysis. A sample may preferably be "drawn" whereby, having chosen a procedure or proportional selection of the material, the laws of probability govern the securing of a representative sample; more rarely it may be "selected." If the latter, a high degree of knowledge of the history, character, use, et cetera, may govern. Contrariwise reliance on pure blind chance may be sufficient or, more rarely, desirable.
>
> Drawn samples are almost invariably indicated where payment is to be made on the quantity factor as in raw materials or by-products and intermediate products.
>
> Selected samples are more often employed for finished products where mutilation or destruction will ensue with considerable attendant money loss. They

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[1] PERRY, *op. cit.*, pp. 1746–1757.

[2] Lucius Pitkin, Inc., New York.

apply more to mechanical rather than chemical products but even there are often mistakenly employed.

In selection, however, one may for contrast have purposely as an objective the *obtaining of a sample which is not representative of the whole but does emphasize unhomogeneity*. As an example the development of a routine sampling method may involve not only reliance, within permissible cost, upon the laws of probability but may involve considerable experimental sampling wherein deliberate selection of heterogeneous phases is necessary to complete the picture. This particular use of selection serves to stress the dangers attendant on its use as a routine method.

When drawn, governing factors (often in some such order of importance as here given) are

1. Percentage to be taken.
2. Use to which subsequent analysis is to be put.
3. Character of material (whether homogeneous or prone to segregation, or whether wet or dry).
4. Value or economics of the materials (permissible cost of sampling).
5. Equipment facilities available (automatic or hand).
6. Skill and experience of personnel involved.
7. Chemical changes which could occur during sampling and must be avoided or minimized.
8. Reconciliation of sample for chemical analysis with that for physical tests. In metallurgy for instance they are not necessarily one and the same.

In some cases the chemical changes that may occur (often by oxidation and aside from loss of moisture) between the formation or shipment of the product and the sampling upon receipt may be of considerable moment and a cause of misunderstanding between seller and buyer or production and inventory control. Flotation sulfide concentrates are an example. Or the heat generated in a pulverizer or other similar attrition mill may be serious enough, especially if the optimum moisture condition is present (neither dry nor too wet) to result in volatilizing or oxidizing certain constituents. Iron pyrites is an excellent example.

With some materials the obtaining of a representative sample for moisture is more difficult and more important than that of obtaining the regular sample as it is called. Yet if the sample is adequate for moisture it may or may not follow that it will suffice for the regular. In the case of wet fine or flotation concentrates it definitely should. In the case of a dry but coarse and heterogeneous ore it would not.

Again one must see that the sample for determination of the regular constituents is dried not only at the proper temperature but under similar conditions to that employed for the moisture. Consequently where chemical changes may occur one and the same sample should be taken where possible for both moisture and regular determinations. Here zinc or copper flotation sulfide concentrates also serve as excellent examples.

Sampling for regular control of purchases, production, and deliveries may be cheaper and simpler or it may be more detailed and expensive than that involved in an exploratory, research, or development project. Some material cannot well be sampled "as is." Considerable preparation, reduction in size, or separation into component parts or phases may be obligatory.

On occasion great care must be employed to avoid contamination from atmosphere, containers, or equipment. On others, such as metal alloy products prone to inherent or induced segregation because of both soft and brittle constituents, separation by screening into coarse and fines and ascertainment of the proportions of each may be obligatory.

The examples shown have been confined to solid material but liquids, highly liquid sludges, and emulsions and even gases present their distinctive problems.

By all of which, limited as is this presentation, it may be seen that sampling is an art requiring more knowledgeable supervision, skilled personnel to carry out, and more cooperation between plant departments than is sometimes realized. To repeat the opening sentence, no analysis, no matter how adequately performed, can be better than the sample.

CONTAINERS

The most economical containers are the refillable bulk ones such as tank cars, boxcars, gondola cars, barges, or even tank steamers. Under this class might even come pipe lines for the transportation of oils, acid, or brine. Coal is shipped in bulk containers and stored in bins in houses or in stock piles in factories. The United States has been most progressive in the development of bulk means of transportation such as are now used not only for coal, oil, and gasoline but also for alcohol, molasses, sulfur, soda ash, nitric acid, sulfuric acid, hydrochloric acid, caustic soda, liquid ammonia, and many other chemicals. Tank and boxcars or barges make many trips between seller and purchaser and afford a very low-cost container. The railroad car is low in its original capital cost as well as in its handling expense.

Many chemicals are shipped in smaller containers which may be either of the returnable or of the one-trip variety. Among the *returnable* containers are

Metal drums, 55 and 100 gal., for acids, oil, solvents, and many liquids.
Steel cylinders, for compressed gas such as hydrogen and oxygen and for liquids such as ammonia and carbon dioxide.
Wooden barrels, 50 gal., for very many liquids and solids.
Wooden kegs, 1 to 10 gal., for very many liquids and solids.
Glass carboys, 12 gal., for acids and other liquids.
Glass demijohns, 1, 2, and 2½ gal., for liquids.
Glass-stoppered acid bottles, usually about 1 gal. or smaller.
Cotton bags for cement.

Among the nonreturnable or *one-trip* containers may be listed the following:

Thin steel drums, for caustic soda, asphalt, and tar.
Fiber drums, for solid chemicals.

Fiber[1] cans, for small amounts of solid chemicals.
Cotton bags, for soda ash, salt, and many bulk chemicals.
Light wooden barrels, for solid chemicals.
Light wooden boxes and crates, mostly for protecting other containers.
Paper sacks, lined or multiwalled, for even hydroscopic chemicals.
Tinned or other thin metal cans, for liquids or solids.
Small glass bottles of various sizes, for very many solid and liquid chemicals.

The choice of a suitable container is often one for a specialist.[2] Many containers are lined with paper, which may or may not be waterproofed. Other containers are given a protective inner coating of sodium silicate, glue, lacquer, or paraffin.

The cost of containers varies from 6 to 10 cents for paper bags, around $1 for wooden barrels for solids, $3 to $4 for iron drums, $4.50 for glass carboys, $11 for steel cylinders, up to around $3,000 to $4,000 for 10,000-gal. low-pressure tank cars, or $6,000 to $7,000 for high-pressure cars used in transporting such gases as helium. To reduce the cost of container and handling and to effect a saving of warehouse space, the use of multiwalled heavy-duty paper containers[3] is on the increase. This is expected to be carried over into the postwar period because of the now demonstrated economies.

TABLE 1.—METHODS OF TRANSPORTATION FOR THE CHEMICAL INDUSTRIES[a]

Inbound shipments				Outbound shipments			
Material	Tons	Per cent	Via	Product	Tons	Per cent	Via
Solid fuels and raw materials	230,000,000	77	Railway	Solids . . .	180,000,000	82	Railway
Liquid fuels and raw materials.	175,000,000	17	Waterway	Liquids. . .	125,000,000	12	Waterway
		6	Highway	Gases. . . .	1,000,000	6	Highway

[a] *Chem. & Met. Eng.*, **44**, 557 (1937).

It is estimated[4] that the chemical industries spend annually $1,000,000,000 for transportation and $500,000,000 for shipping facilities, packing, and containers. Table 1 summarizes the methods of transportation.

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[1] BIGGER, Fiber Cans, Alternates for Metal Containers, *Chem. Eng. News*, **21**, 1436 (1943).

[2] *Chemical and Engineering News* is conducting a periodic department headed "Packaging" under the leadership of Richard W. Lahey. This is devoted to the various phases of packaging, such as production, improvements, availability, new inventions, and governmental statistics and regulations. See also a similar periodic department, called "Packaging and Shipping" by T. P. Callahan in *Chemical Industries*.

[3] ANON., Bulk Packaging of Chemicals, *Chem. & Met. Eng.*, **50**, No. 10, 117 (1943).

[4] *Chem. & Met. Eng.*, **44**, 557 (1937).

Under the unit operation of *movement and storage of materials*, occurs the subdivision of *bulk-packing equipment* wherein the chemical engineer handles the equipment needed to put his product economically into a barrel, drum, or sack. Perry[1] presents this with regard to the various laborsaving and automatic devices that are in use.

SAFETY AND FIRE PROTECTION

The superintendent of a chemical factory pays much attention to the safety of his men and to protection against fire. Safety measures not only keep an employee regularly on the job and the equipment working but actually save money in the reduction of the premiums paid by employers for liability and fire insurance. One of the principal jobs of the chemical engineer is the establishment of adequate safety measures to protect workmen and also the chemical engineer himself.

TABLE 2.—DISABLING INJURIES, 1939, CHEMICAL INDUSTRY, BY INDUSTRIAL GROUPS[a]

Industrial group	Number of industrial units	Man-hours worked (thousands)	Average number of employees	Number of disabling injuries				Injury rates	
				Death and permanent, total	Permanent, partial	Temporary, total	Total	Frequency	Severity
All groups	417	305,535	144,378	40	172	2,073	2,285	7.48	1.26
Laboratories	13	4,202	2,062	0	0	3	3	0.71	0.003
Industrial gases	8	4,303	2,109	1	1	5	7	1.63	1.43
Alcohol and solvents manufacturing	5	2,010	951	0	0	7	7	3.48	0.06
Plastics manufacturing	16	13,485	6,704	0	15	36	51	3.78	0.38
Acid manufacturing	40	19,739	9,623	4	16	56	76	3.85	1.82
Chlorine and alkali manufacturing	12	15,206	6,645	2	3	57	62	4.08	0.96
Carbon products	13	9,397	4,629	1	12	35	48	5.11	1.44
Dye manufacturing	7	11,602	5,752	1	7	56	64	5.52	0.91
Paint and varnish manufacturing	37	21,864	10,742	1	4	136	141	6.45	0.47
Pharmaceutical and fine chemical manufacturing	29	43,631	15,977	3	13	377	393	9.01	0.77
Explosives manufacturing	59	27,702	13,822	11	20	253	284	10.25	3.00
Soap manufacturing	31	24,760	12,556	2	32	234	268	10.82	1.32
Coal-tar distillers	17	1,155	558	1	0	16	17	14.72	5.39
Fertilizer manufacturing	12	8,150	4,018	3	6	122	131	16.07	3.19
Salt manufacturing	12	4,340	2,163	0	2	74	76	17.51	0.51
Vegetable oil manufacturing	30	7,609	3,850	0	9	131	140	18.40	1.42
Not otherwise classified	76	86,380	42,217	10	32	475	517	5.99	1.09

[a] *Chem. & Met. Eng.*, **47**, 703 (1940). The results for 1939 are more normal than for the later war years.

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[1] PERRY, *op. cit.*, pp. 2293–2322.

Too frequently, familiarity with chemicals breeds carelessness. To ensure against this attitude, well-run plants have safety committees in which men from other departments check up the safety devices and recommendations of those actually working with the given process. There is only one thing more disturbing than a bad accident and that is a conflagration. Although both can be insured against, it is cheaper and interrupts production less to prevent such accidents or fires.

Adequate safety and fire protection measures require expert guidance. Whereas much information[1] is available in the literature, more specific help can be obtained from the National Safety Council,[2] a cooperative organization for the purpose of disseminating information among its members and of promoting safety in all its aspects.

Table 2 summarizes the disabling injuries met with throughout the chemical industries. Certain companies by proper organization and training have greatly reduced the number and severity of harmful accidents to life, limb, and plant. This is true of even those industries which are inherently dangerous.

The National Safety Council, reporting on 400 accidents in 1942, tabulates the following causes:

Agency of Injury	Number of Injuries
Presses, rolls, and other machinery	139
Acids, alkalies, and other chemicals	44
Floors, ladders, and other working surfaces	34
Trucks, railroad cars, and other vehicles	33
Pipe lines, boilers, and other pressure apparatus	27
Elevators, cranes, and other hoisting apparatus	22
Hand tools	17
Conveyers	14
Mechanical power transmission apparatus	11
Other	59
Total	400

From this tabulation it is seen how very important it is to continue training men to protect themselves from moving machinery as well as from chemicals. Unsafe practices caused 85 per cent of these 400 injuries. Some of these unsafe practices are cleaning, adjusting, or repairing in the vicinity of moving machinery, using defective machinery or tools, starting or stopping machinery without signaling other workmen, standing under suspended loads or assuming unsafe positions, failure to wear protective devices such as goggles or safety shoes, entering dangerous areas, removing safety devices, mixing chemicals to cause explosion or fire.

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[1] PERRY, *op. cit.*, 2873–2950, excellent presentation with bibliography; ANON., Safety and Fire Prevention in the Chemical Industry, *Chem. & Met. Eng.*, **47**, 700 (1940); HUFF, Protection of Pressure Vessels with Rupture Discs, *Refrig. Eng.*, **46**, No. 5, 312–315 (November, 1943).

[2] 20 North Wacker Drive, Chicago.

Equipment should be tested[1] initially and periodically to ensure safety and efficiency. The chemicals handled most frequently have certain hazardous aspects, which should be ascertained and guarded against. Flammable liquids[2] can be safely processed. Specific chemicals, such as ammonia[3] and hydrofluoric acid[4] and many others that are hazardous, can be so handled by the chemical engineers who are conversant with their properties that safety of plant and of workman can be secured.

PATENTS

In order to encourage new discoveries for the benefit of the nation the Constitution provides for patents. These are limited monopolies extending over 17 years and given in exchange for something new and beneficial. However, as it takes an average of about 7 years between the time an invention is patented until it is commercialized, the monopoly exists practically for only about 10 years. After this the public has a right to use the invention freely. Patents are necessary in this competitive system of free enterprise in order that research funds can be generously spent for improvements on old processes and for new and useful discoveries. The system of inventions enables a concern to reimburse itself for its large expenditure for research. The American patent system also discourages secret processes by guaranteeing the limited monopoly only in case of an adequate disclosure. There is no quicker way to have a patent declared invalid than to show before an impartial court that an inventor has held back some essential step in the disclosure of his idea.

Dean A. A. Potter, as Executive Director of the National Patent Planning Commission, writes the following about patents:[5]

> A clear understanding is essential of the difference between an invention, a patent, and a marketable product. Invention is the act of finding something that is new. A patent is a grant of exclusive right to the inventor to his invention for a limited period of time. An invention is not a product, and the patent by

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[1] DUGGAN, How Carbide Tests Equipment to Prevent Accidents, *Chem. & Met. Eng.*, **47**, 678 (1940).

[2] GRIFFIN, Guarding against the Flammable Liquid Fire Hazard, *Ind. Eng. Chem.*, **34**, 664 (1942).

[3] BRANDT, Storage and Handling of Anhydrous Ammonia in Tank Car Quantities, *Chem. Industries*, **53**, 200 (1943).

[4] FEHR, The Safe Handling and Storage of Hazardous Hydrofluoric Acid, *Chem, Industries*, **53**, 505 (1943); *Petroleum Refiner*, **22**, 239 (1943).

[5] POTTER, The Engineer and the American Patent System, *Mech. Eng.*, **66**, 15–20 (1944).

itself does not produce a product. To produce a marketable product a new idea in the form of an invention must be developed and embodied in a form suitable for manufacture, and appropriate tools must be available so that the product can be manufactured at a cost acceptable to the public. The patent serves to protect the inventor and those who develop, manufacture, and sell the product from the uncontrolled competition of parties who have not shared the burden of invention and its commercialization.

Inventions, by bringing these new products to the commercial world, benefit the public at large and *for all time.* The inventor himself receives only a *limited* reward. The inventor, however, *creates* something that did not exist before. In the field of the chemical industries, the American patent system is accountable for much of the recent growth by encouraging the research upon which this growth is founded. The obtaining of a patent is a procedure requiring skilled and experienced guidance. The patent office does not require that an inventor proceed with the help of a patent attorney but sound business judgment does. The patent must be of something *new* and must be fully *disclosed,* and the essentials of the invention must be properly covered by the *claims.* There are also a number of pitfalls that an inexperienced inventor might fall into, such as attempting to cover more than one invention in one patent or not keeping the necessary records of the conception of his invention or of its reduction to practice. All these requirements, and more too, are largely avoided by the association of reputable patent counsel with the inventor.

RESEARCH

It is certainly true that adequate and skilled research with patent protection guarantees future profits. In the chemical process industries some of the outstanding characteristics are changing procedures, new raw materials, new products, and continual increase from laboratory test tube to tank car shipments. Research creates or utilizes these changes. Without this forward-looking investigation or research, a company would be left behind in the competitive progress of the industry. A company might possibly have so fundamental a raw material and such a well-developed process that research could not improve the product. Though this latter statement is rarely true, it is a fact that the progress of industry opens up new markets for even the most fundamentally established products. The results and benefits of research[1] may be tabulated as follows:

1. New and improved processes.
2. Lower costs and lower prices of products.
3. New services and new products never before known.

[1] *Chem. & Met. Eng.*, **44**, 545 (1937).

4. Change of rarities to commercial supplies of practical usefulness.
5. Adequate supply of chemicals previously obtained only as by-products.
6. Freedom for American users from foreign monopoly control.
7. Stabilization of business and of industrial employment.
8. Products of greater purity.
9. Products of superior service, *e.g.*, light-fast dyes.
10. New medicines and other new health aids.
11. More efficient use of raw materials.
12. More efficient by-product recovery.

These results, just quoted, may also in their own words be summarized by the expression "creation of new industry and stabilization of old."

As shown in Table 3 of Chap. XXXVIII, the coal-tar products division of chemical industry spends about 3½ per cent of sales on research. The aliphatic division spends a higher proportion because it is a newer and faster developing field. Both the aliphatic and the aromatic spent in 1940 over $16,000,000 in research. The research of the United States is almost an industry in itself, there being over 1,700 laboratories employing over 40,000 workers and spending over $200,000,000 annually.[1] In the field of the chemical process industries, research and development bring out many new products each year, design new equipment, or find new uses for old products. Indeed, the characteristic of this group in American industry is *change*. This, so far, has been synonymous with *improvement* or, in the words of the duPont radio advertising man, "Better things for better living through chemistry." Finally, it may be remarked that, in a business and financial sense, it would be unwise either to work for or to continue to hold the securities of any firm which, in these competitive days, is not research minded.

WASTE DISPOSAL

There was a time when any product that a manufacturer did not want was turned loose into the air or run into the nearest stream irrespective of odor, color, or toxicity. Fortunately these days are past.

However, it is not always an easy procedure to dispose of wastes.[2] Sometimes a long-drawn-out study is required to ascertain how either to neutralize the waste, to destroy it, or to turn it to something useful. Chemical wastes are particularly bothersome because they are so variable in their properties. The colored liquor running from a dyeing establishment should be treated entirely differently from the acid liquors escaping from a coal mine. Hence, the treatment of chemical wastes is largely in the hands of the experienced chemical engineer who must first determine the exact chemical nature of the waste products and its properties. He should then endeavor to prevent its formation or to turn it into something useful. When this is impossible, his efforts should be directed to neutralize economically the harmful effect of the waste so that neither the air nor the rivers are contaminated.

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[1] Vagtborg, Our Research System, *J. Eng. Education*, **31**, 421 (1941).

[2] Snell and Fain, Chemical Treatment of Trade Waste, *Ind. Eng. Chem.*, **34**, 970 (1942); Mohlman, Industrial Waste Disposal, *Chem. & Met. Eng.*, **50**, No. 2, 127 (1943).

MISCELLANEOUS ASPECTS

Whereas the first part of this chapter has considered in more or less outline the general fundamentals in connection with the operation of chemical plants, there are many other aspects of importance, among which are plant location, consideration of competing processes, the labor market, and the sales outlet. Furthermore, every growing concern should have a number of adjuncts to its manufacturing operations among which may be mentioned an efficient pilot plant and a library.

Plant Location.[1]—Naturally, the proper location for a chemical plant or a branch plant is conditioned largely by raw materials, transportation, and markets. Yet, many other factors appear, such as power, water, availability of efficient labor, cost of land, and ability to dispose of wastes. There is a very strong tendency on the part of chemical concerns to leave congested cities and to move out either into smaller towns or actually into the country.

Competing Processes.—As change is almost the outstanding characteristic of chemical procedures, this phase of any process is not only of importance when the plant is first designed but should be always in the consciousness of any chemical executive. Indeed, one of the functions of a research organization is to keep abreast with the progress of the basic sciences and to make available for the organization any improvements or even fundamental changes leading to the making of any given product in which the organization is interested. The research organization should also keep informed regarding developments in other companies and be in a position to advise the executives of the relative competitive position of actual or contemplated processes or products.

Labor.—The conduct of chemical plants requires, as a rule, rather skilled labor with a limited requirement for ordinary backbreaking work. Most of the help needed is for men who can repair, maintain, and control the various pieces of equipment necessary to carry out the *unit processes* and the *unit operations*. As each year passes, the chemical industry by virtue of a wider use of instruments and a greater complexity of equipment requires more and more of the higher type of skilled labor.

Sales.—There is no reason to manufacture anything unless it can be used or sold. In order to sell goods properly in these competitive times, "sales service" must frequently accompany the delivery of the manufactured article. A customer can be shown more appropriately how to use a given product by the salesman fully acquainted with its properties. An understanding of the customer's problems often helps in planning manufacturing operations. By reason of these sales aspects many chemically trained men are entering sales or sales service as their life work.

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[1] PERRY, *op. cit.*, pp. 2832–2840.

Pilot Plants.—No new process should be moved from the laboratory into the plant without going through a pilot plant. A good principle is to insist that the product be made first on the small scale. It is much cheaper to make errors and quicker to correct them when operating in a pilot plant than in the factory. Furthermore, if a new venture is being undertaken, it is difficult to design the large-scale procedure effectively without having first run the process in a small pilot plant. There the equipment should be made out of the same materials as the best engineering judgment indicates should be chosen for the large plant. There, also, the corrosion, wear, and tear on these materials can actually be observed under small-scale manufacturing conditions. In the pilot plant the installation should be of *replica* equipment usually on the smallest scale available. The pilot plants also serve to train foremen for the factory procedures.

Library.—Any plant of any size should have available present and past literature, in its field as well as the records of its past experience. In the library there should be collected and made available statistics[1] pertaining to the domestic manufacture and imports of any products the company makes or is considering.

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CHAPTER IV

WATER CONDITIONING AND WASTE-WATER TREATMENT

Water conditioning and waste-water treatment have long been essential functions of municipalities. However, the importance of suitably preparing water for the chemical industry is sometimes overlooked, although the chemical manufacturing processes consume enormous quantities of water ranging in quality from untreated to distilled.[1] Industrial water wastes present a greater disposal problem than municipal wastes. No single method is applicable for the treatment of chemical wastes because of their widely differing physical and chemical characteristics. A chemical plant may use as many as six different waters, as shown in the following listing[2] for the Calco Chemical Co. at Bound Brook, N. J., where the consumption is 10,000,000 gal. per day:

1. River water, pumped from the Raritan, which is the ordinary manufacturing water of most of its operations.
2. Well water from the company's own artesian wells, esteemed for its low temperature and its purity—very useful in cooling.
3. Filtered water, from the company's filtration plant, required in a great number of processes.
4. Treated water, precipitated with alum and softened with trisodium phosphate, which must be handled in copper pipes, as it is contaminated in iron or brass.
5. Distilled water, for the laboratories and for all testing work, which is circulated to needed points in pure block-tin pipes.
6. Potable water for the drinking and cooking supplies.

As is well known, the purity and the quantity of available water are very important in the location[3] of a chemical plant. Both the surface and the ground water should be considered. The latter is more suitable usually for cooling purposes because of its uniformly low summer and winter temperature, but such water is generally harder, may cause scale, and hence may interfere with heat transfer.

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[1] Hall, Water as Raw Material for Chemical Industries, *Chem. & Met. Eng.*, **38**, 513–515 (1931); Montgomery, How Process Industries are Meeting Their Water Supply Problem, *Chem. & Met. Eng.*, **47**, 622–625, 680–684, 840–843 (1940).

[2] Anon., "Dyes Made in America 1915–1940," Calco Chemical Division, American Cyanamid Co. This company also has a zeolite water-softening plant. *Cf.* King, Bean, Lester, and Rudolfs, Water Treatment of the Calco Chemical Division, *Chem. Eng. News*, **21**, 1046 (1943).

[3] Perry, *op. cit.*, p. 2835.

The impurities contained in water[1] vary greatly from one section of the country to another. Hard waters are those containing objectionable amounts of dissolved salts of calcium and magnesium. These are present as bicarbonates, chlorides, or sulfates. These salts give insoluble precipitates with soap and form clogging scales with low thermal conductivities when used in boilers.

Hardness is usually expressed in terms of the dissolved calcium and magnesium salts calculated as calcium carbonate equivalent, $CaCO_3$; when these constituents are measured by titrating with a standard soap solution, this is frequently called *soap hardness.* The common units used in expressing water analyses are parts per million (p.p.m.) and grains per gallon. One grain per gallon is equivalent to 17.1 p.p.m. Water hardness may be divided into two classes: *carbonate* and *noncarbonate,* also frequently known as *temporary* and *permanent.* Temporary hardness can usually be greatly reduced by boiling; permanent hardness requires the use of chemical agents. Carbonate or temporary hardness is caused by bicarbonates of lime and magnesia; noncarbonate or permanent hardness is due to the sulfates and chlorides of lime and magnesia. In addition to hardness, there may also be present varying amounts of sodium salts, silica, alumina, iron, or manganese. The total dissolved solids may range from a few parts per million in snow water to several thousand parts per million in water from mineral springs. Other water impurities that may be present are suspended insoluble matter (classed usually as turbidity), organic matter, color, and dissolved gases. Such gases are carbon dioxide (largely as bicarbonate), oxygen, nitrogen, and, in sulfur waters, hydrogen sulfide.

WATER CONDITIONING

Water conditioning must be adapted to the particular use for which the water is designed. It is furthermore a complicated phase of chemical engineering practice, and problems should be referred to the experts in this field. The use of elevated pressures (now up to 1,400 lb. per sq. in.

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[1] Typical water analyses are tabulated in many books and articles. See CLARKE, Composition of River and Lake Waters of the U.S., *Prof. Paper* 135, U.S. Geological Survey, Washington; CERNA, Industrial Water Conditioning Processes, *J. Chem. Education,* **20,** 108 (1943). Maps showing hardness of surface waters and of ground waters for the United States are given by Olson, Benefits and Savings from Softened Water, *J. Am. Water Works Assoc.,* **31,** 609–611 (1939); MONTGOMERY, How Process Industries are Meeting Their Water Supply Problems, *Chem. & Met. Eng.,* **47,** 622–625 (1940). See also, MASON and BUSWELL, "Examination of Water," 6th ed., John Wiley & Sons, Inc., New York, 1936; COLLINS, Natural Waters Available for Industrial Use, *Chem. Eng. News,* **21,** 1062 (1943).

and higher for steam generation) requires the employment of more carefully purified boiler feed water. And each industry[1] has its special water-conditioning requirements, *e.g.*, the laundries require zero hardness to prevent precipitation of calcium and magnesium soap on the clothes. Likewise calcium and magnesium salts cause undesirable precipitates with dyes in the textile industries or with the dyes in paper manufacture.

Historical.—In this country an abundance of fairly soft water has long been available from surface supplies of the industrial Northeast. Cities such as New York and Boston obtain comparatively soft water from rural watersheds over igneous rocks. However, as the Middle West and the West were developed, it became necessary to use the harder water that prevails in these limestone areas. This hard water needs to be softened for many [illegible]es. Furthermore, as the advantages of really soft water are recognized, more and more even fairly soft waters are being *completely softened* for laundries, homes, and textile mills.

Thomas Clark of England, in 1841, patented the lime process for the removal of carbonate or temporary hardness. A short time after Clark's patent, Porter developed the use of soda ash in removing the noncarbonate or permanent hardness of water. In spite of earlier work by Thompson, Way, and Eichhorn on zeolite base exchange, it was not until 1906 that Robert Gans, a German chemist, applied zeolites to actual commercial use for water-softening purposes. The two earliest softening plants for an entire city supply were installed at Canterbury and Southhampton, England, about 1888.[2] Only during the last 10 years of the century of availability has softening been extended to municipal supplies in any appreciable extent. The explanation may be that many people, lacking in experience with water other than hard waters, were ignorant of the advantages of softened water. Table 1 shows the varying hardness of waters in use in the United States.

TABLE 1.—VARYING HARDNESS OF WATERS USED IN THE UNITED STATES IN 1932[a]

Range of Hardness, p.p.m.	Per Cent of Total Population
1- 60	29.5
61–120	26.9
121–180	15.3
More than 180	10.4

[a] OLSON, *op. cit.*

METHODS OF CONDITIONING WATER

The purification and softening of water may be accomplished by different methods. Table 2 presents a summary of the principal water-softening processes. The use to which the water is to be put determines, frequently, the treatment chosen. *Softening* is the term applied to those processes which remove or reduce the hardness of the water. *Purification*, as distinguished from softening, usually refers to the removal of organic matter and microorganisms from the water.

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[1] FURNAS, "Rogers' Manual of Industrial Chemistry," 6th ed., pp. 199–205, D. Van Nostrand Company, Inc.

[2] OLSON, Benefits and Savings from Softened Water, *J. Am. Water Works Assoc.*, **31**, No. 4, 612 (1939).

TABLE 2.—SUMMARY OF WATER-SOFTENING INSTALLATIONS IN THE UNITED STATES FOR 1940[a]

Type and Field	Number
Zeolite, household	300,000
Zeolite, industrial	35,000
Zeolite, municipal	170
Chemical precipitation, industrial	3,000
Chemical precipitation, municipal	364

[a] *Private communication*, Eskel Nordell of the Permutit Co. See OLSON, *op. cit.*, p. 615. The chemical precipitation type includes cold and hot lime-soda installations.

Zeolite Softening Process.—The most important method for softening water is the zeolite or cation-exchange system. Zeolite is the name applied to a class of hydrated alumino-silicates that contain easily exchangeable ions such as sodium or potassium. During the softening process, the Ca and Mg ions are removed from the hard water by the zeolite and replaced by the Na ions. When the zeolite becomes almost all changed to calcium and magnesium compounds, it is regenerated by treatment with an excess of brine, thus restoring the sodium zeolite. Typical equations for this type of softening are, where Ze represents a zeolite,

$$Na_2Ze + Ca(HCO_3)_2 \rightarrow CaZe + 2NaHCO_3 \qquad (1)$$

$$Na_2Ze + CaCl_2 \rightarrow CaZe + 2NaCl \qquad (2)$$

These zeolites are either natural or artificial products and may be expressed by the generalized formula $Na_2O \cdot R_2O_3 \cdot nSiO_2 \cdot xH_2O$ where R_2O_3 is either Al_2O_3 or Fe_2O_3, n represents 5 or more, and x varying amounts of water of hydration. Similar reactions may be written for magnesium salts. For regeneration the reaction is

$$CaZe + 2NaCl\ (\text{excess}) \rightarrow Na_2Ze + CaCl_2 \qquad (3)$$

The equipment for the process, as shown in Fig. 1, is a large, closed cylindrical tank in which the zeolite is supported on graded gravel. The water to be softened may flow down through the tank. Auxiliary apparatus includes both brine and salt storage tanks. The washing and regeneration may be carried out automatically as well as manually. These softeners are installed in the water lines and operated under whatever water pressure is necessary. As the zeolite bed also exerts a filtering action, any sediment from the water or from the salt must be washed off by an *efficient backwash.* This step suspends and hydraulically regrades the zeolite bed

The water from zeolite treatment is usually practically zero in hardness. In cases where very hard water is encountered, it is often desirable to treat the water first by the lime process and follow this by a zeolite unit. The lime process actually *removes* bicarbonate hardness from the water while the zeolite process *exchanges* Ca and Mg ions with Na ions.

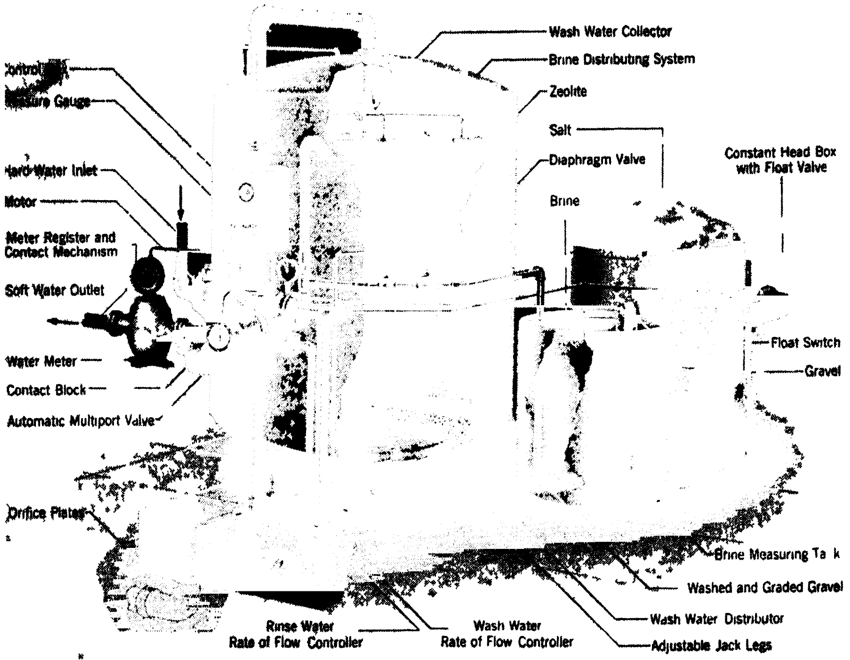

FIG 1 —Automatic zeolite softener (*Courtesy of The Permutit Company*)

Two types of zeolites are employed commercially: (1) a treated, stabilized, and rugged product derived from natural greensand (glauconite) which has a base exchange capacity of 3,000 to 5,000 grains of calcium carbonate hardness per cubic foot and (2) the various synthetic zeolites which are not so rugged but are more powerful, having a base exchange capacity of 8,000 to 12,000 grains per cu ft. These larger capacity artificial zeolites are frequently preferred in household or other softeners where space is at a premium and where their sensitiveness to attack is not so important.

The great advantage of the zeolite softeners is their convenience and the fact that they furnish a water of zero hardness *without attention* or *adjustment* until regeneration is required even though the raw water varies in hardness from one day to the next.

Deionizing or Demineralizing Process.—Synthetic ion-exchange materials are now available that operate satisfactorily to remove completely the dissolved salts from ordinary water and are an extension of the long-used zeolite procedures. These products may be divided into two classes: cation exchangers and anion exchangers.

The new *cation exchangers* are mostly of organic origin and may be roughly divided into

1. Sulfonated natural organic materials like coal, coke, charcoal, lignite, and wood shavings.
2. Synthetic organic resins containing active sulfonic groups and derived frequently from phenol-formaldehyde[1] or polystyrene resins.

These contain an exchangeable hydrogen ion and can be employed to remove all cations according to the following reactions:

$$Ca(HCO_3)_2 + 2HSO_3R \rightarrow Ca(SO_3R)_2 + 2CO_2 + 2H_2O \qquad (4)$$

The acid formed, H_2CO_3 in this case, decomposes and can be removed easily. A similar reaction would be true for magnesium or sodium bicarbonates. Sulfates and chlorides react as follows:

$$CaSO_4 + 2HSO_3R \rightarrow Ca(SO_3R)_2 + H_2SO_4 \qquad (5)$$
$$NaCl + HSO_3R \rightarrow NaSO_3R + HCl \qquad (6)$$

The regeneration is usually effected by sulfuric acid as follows:

$$Ca(SO_3R)_2 + H_2SO_4 \text{ (excess)} \rightarrow 2HSO_3R + CaSO_4 \qquad (7)$$
$$2NaSO_3R + H_2SO_4 \text{ (excess)} \rightarrow 2HSO_3R + Na_2SO_4 \qquad (8)$$

Such cation exchangers are naturally rugged and also possess considerable exchange capacity, up to 16,000 grains per cu. ft. Their application is shown in Fig. 2. If these cation exchangers are regenerated by sodium chloride, instead of acid, they function like the ordinary zeolite softeners.

Acidic water is not desirable for most purposes and, therefore, the effluent from the cation-exchange treatment is either neutralized or, if demineralization is required, is passed through an anion-exchange material, as shown in Fig. 2. Such anion exchangers are for the most part basic resins, being condensation products of amines with formaldehyde.[2]

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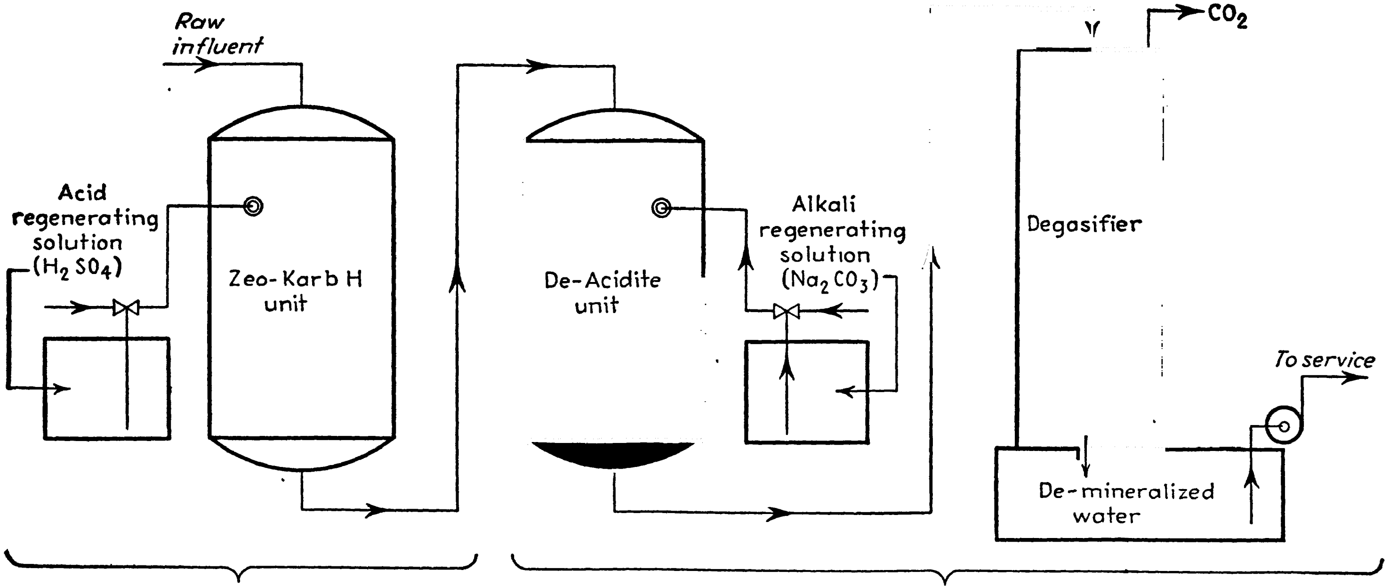
[1] WASSENIGER and GRIESSBACH, U.S. Pat. 2195196 of Mar. 26, 1940.

[2] WALTON, Ion Exchange between Solids and Solutions, *J. Franklin Inst.*, **232**, 305 (1941), excellent presentation with 79 references; TIGER and SUSSMAN, Demineralizing Solutions by a Two-step Ion Exchange Process, *Ind. Eng. Chem.*, **35**, 186 (1943); MYERS, Ion Exchange Resins, *Ind. Eng. Chem.*, **35**, 859 (1943).



Step No 1

Replacement of metallic cations by hydrogen (H ion) converts salts present in raw water into corresponding acids, viz. HCl, H_2SO_4, H_2CO_3

Step No. 2

Removal of acids formed in Step No. 1

The HCL and H_2SO_4 are absorbed in the de-acidite unit and the H_2CO_3 decomposes into H_2O and CO_2, this CO_2 escaping to the atmosphere in the degasifier

FIG. 2.—Two-step process for demineralizing water. The cation unit is rubber lined and the anion unit is asphalt coated to eliminate corrosion. (*Courtesy of The Permutit Company.*)

The reactions may be represented, including regeneration,

$$R'_2NR'' + HCl \rightarrow R'_2N(HCl)R'' \qquad (9)$$

$$2R'_2N(HCl)R'' + Na_2CO_3 \text{ (excess)} \rightarrow 2R'_2NR'' + 2NaCl + H_2O + CO_2 \qquad (10)$$

The *R*'s may be hydrogen.

This dual treatment completely deionizes the water. The equipment necessary for the application of anion and cation exchangers is very similar to that used in zeolite softening except for the necessary acid proofing. If both cation and anion exchangers are employed, two chambers are necessary—one for each step. Figure 2 shows the operations in the two-step process.

The ion-exchange resins, because of ability to deionize and not merely soften water, are now competing with distillation as a means of producing pure water. The final composition of water after the two-step treatment varies somewhat with the quality of the original water. Table 3 gives the average analysis of effluent.

TABLE 3.—ANALYSIS OF EFFLUENT FROM TWO-STEP ION-EXCHANGE TREATMENT[a]

Expressed as p.p.m. as $CaCO_3$:	
Total hardness	0–2
Alkalinity to methyl orange	1–6
Chlorides	0–4
Sulfates	0–3
Free CO_2, p.p.m	5–10

[a] TIGER and SUSSMAN, Demineralizing Solutions by a Two-step Ion Exchange Process, *Ind. Eng. Chem.*, **35**, 186 (1943).

The only other process for removing all the ions in water, other than the two-step ion-exchange method, is *distillation.* Both distilled water and deionized water should be handled in special pipes to keep the soft water from dissolving small amounts of the metal and thus becoming contaminated. Block tin has been employed for this purpose for many years but has the disadvantage of extreme softness. Aluminum and molded polyvinylidine chloride pipes have recently been used for conducting "pure" water and show promise of being as satisfactory as tin.

Lime-soda Process.—The use of slaked lime and of soda ash to remove hardness in water has long been important. The modern application has been divided into the cold lime process and the hot lime-soda process. The calcium ions in the hard water are removed as $CaCO_3$ and the magnesium ions as $Mg(OH)_2$. Typical equations for these reactions are

For carbonate hardness,

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow \underline{2CaCO_3} + 2H_2O \qquad (11)$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow MgCO_3 + CaCO_3 + 2H_2O \qquad (12)$$

Then, since the $MgCO_3$ is fairly soluble,

$$MgCO_3 + Ca(OH)_2 \rightarrow \underline{Mg(OH)_2} + \underline{CaCO_3} \tag{13}$$

For noncarbonate soluble calcium and magnesium salts,

$$MgCl_2 + Ca(OH)_2 \rightarrow \underline{Mg(OH)_2} + CaCl_2 \tag{14}$$

$$CaCl_2 + Na_2CO_3 \rightarrow \underline{CaCO_3} + 2NaCl \tag{15}$$

$$CaSO_4 + Na_2CO_3 \rightarrow \underline{CaCO_3} + Na_2SO_4 \tag{16}$$

$$MgSO_4 + Na_2CO_3 + Ca(OH)_2 \rightarrow \underline{Mg(OH)_2} + \underline{CaCO_3} + Na_2SO_4 \tag{17}$$

From these reactions it is apparent that, for carbonate hardness, each unit of calcium bicarbonate requires one mole of lime while for each unit of magnesium bicarbonate there is needed *two* moles of lime. For noncarbonate hardness, likewise, the magnesium salts require more reagents (one mole each of soda ash and lime) while the calcium salts require only one mole of soda ash.

Based on a price of $10 per ton for lime (quicklime of 90 per cent purity) and of $30 per ton of soda ash (98 per cent purity), the following costs have been figured[1] for removing 100 p.p.m. of hardness from 1,000,000 gal. of water.

Calcium bicarbonate hardness (expressed as $CaCO_3$), 520 lb. lime	$2.60
Magnesium bicarbonate hardness (expressed as $CaCO_3$), 1,040 lb. lime	5 20
Calcium noncarbonate hardness (expressed as $CaCO_3$), 900 lb. soda ash	13.50
Magnesium noncarbonate hardness (expressed as $CaCO_3$), 900 lb. soda ash 520 lb. lime	16.10

The *cold lime* process is employed chiefly for partial softening and ordinarily uses only the cheaper lime for its reagent [reactions (11) to (14) above]. It reduces the calcium hardness to 35 p.p.m. if proper opportunity is given for precipitation of the hardness, thus discharging the "supersaturation" so frequently met with in this process. This cold lime process is particularly applicable to partial softening for municipal water (Figs. 4 and 5), to the conditioning of cooling water where calcium bicarbonate hardness may be the scale former and to certain paper-mill waters where calcium bicarbonate is troublesome. The magnesium carbonate hardness can be removed to any desired or economical amount but, if a low residual is wanted, an excess of hydroxyl ions is needed to depress the solubility of the magnesium hydroxide. Usually to aid in the precipitations, a coagulant, aluminum sulfate, is added to lessen afterdeposit.

The newest and most successful method of eliminating *supersaturation* in the cold lime-soda process is contacting previously precipitated sludge (see Fig. 4). When this material is exposed to the raw water and chemicals, the like surfaces or "seeds" accelerate the precipitation. The result is a more rapid and more complete reaction with larger and more easily settled particles in the newly formed precipitate. Various equipment has been recommended for this step.

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[1] ANON., "Water Conditioning Handbook," Permutit Co., New York, 1943

The equipment developed for this contact by the International Filter Company is called the *Accelerator*.[1] In this apparatus there is a special device for mixing the treating chemicals with the suspension of the previously precipitated sludge. Following this, the raw water is introduced into the mixture of chemically impregnated slurry whereupon the positive contact of solid particles and water to be softened with the softening chemicals affords an improved opportunity for precipitation of calcium carbonate and magnesium hydroxide, thus resulting in "desupersaturation."

The Permutit Spaulding Precipator[2] consists of two compartments: one for mixing and agitating the raw water with the softening chemicals and with the previously formed sludge, and the other for settling and filtering the softened water as it passes upward through the suspended blanket of sludge. Machines of these types reduce sedimentation time from 4 hr. to less than 1 hr. and usually effect savings in chemicals employed. A still newer machine, the Spiractor, has a detention period of about 10 min. and also functions in the cold lime-soda process.[3] In the Spiractor the hard water plus the necessary softening chemicals travels upward and spirally around granules upon which the hardness precipitates.

The *hot lime-soda process* is employed almost entirely for conditioning boiler feed water. Since it is operated near the boiling point of the water, the reactions proceed faster, the coagulation and the precipitation are facilitated, and much of the dissolved gases such as carbon dioxide and air is driven out.

The hot lime-soda treatment for softening may consist of the following coordinated sequences of *unit operations* (Op.) and *unit processes* (Pr.) which are frequently carried out in such equipment, as illustrated by Fig. 3:

Analysis of the raw water (Pr.).

Heating of the raw water by exhaust steam (Op. and Pr.).

Mixing and proportioning of the lime and soda ash in conformance with the raw water analysis (Op.).

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[1] BEHRMAN and GREEN, Accelerated Lime Soda Water Softening, *Ind. Eng. Chem.*, **31**, 128 (1939).

[2] SPAULDING, Conditioning of Water Softening Precipitates, *J. Am. Water Works Assoc.*, **29**, 1697–1707 (1937).

[3] TIGER and GILWOOD, The New Sludgeless Cold Lime Soda Water Softener, *Paper Trade J.*, **113**, No. 13, 27–31 (1942).

Pumping of the lime-soda mixture into the raw water (Op.).

Reacting of the lime soda, facilitated by mixing with or without previous heating (Pr. and Op.).

Coagulation or release of the "supersaturation" by various methods such as slow agitation or contact with "seeds" (Pr. and Op.).

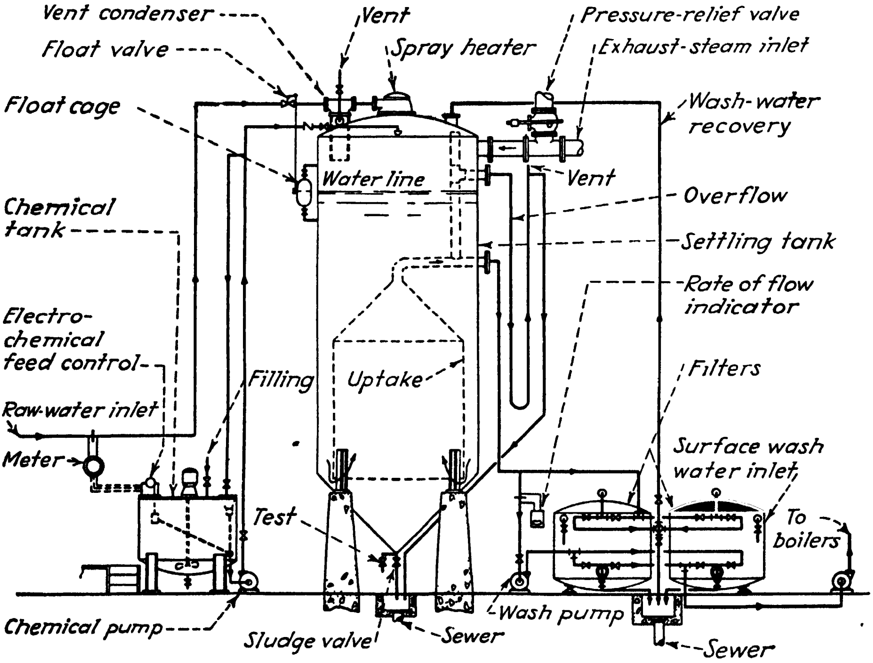

FIG. 3.—Hot lime-soda softener. (*Courtesy of The Permutit Company.*)

Settling or removal of precipitate with or without final filtration (Op.).

Pumping away of softened water (Op.).

Periodic washing away of the sludge from the cone tank bottom (and from the clarifying filters) (Op.).

If the chemical reactions involved could be carried to completion, the hardness of the water would be reduced to the theoretical solubilities of the calcium carbonate and magnesium hydroxide. This would leave a hardness of approximately 20 to 25 p.p.m. in pure water and a little less at the pH of 10 to 11 involved in the lime-soda process. Frequently for feed water, a sodium phosphate treatment follows the lime soda in order to soften the water more completely. This is particularly necessary when feeding high-pressure boilers.

Phosphate Conditioning.—Various phosphates are employed, usually in conjunction with one of the previously described procedures. *Monosodium, disodium,* and *trisodium phosphates* are often added to water to precipitate the hardness ions in the form of easily removed soft phosphate sludges. Sodium hexametaphosphate, $(NaPO_3)_6$,[1] likewise softens water but instead of precipitating the hardness ions it forms soluble complexes with the Ca, Mg, Fe, and Al ions and sequesters them or prevents the formation of scale or insoluble soaps when the phosphate is present in excess and when the water is not too hot. This chemical also possesses the valuable property of dispersing previously formed insoluble soaps. These properties led to the so-called *threshold treatment*[2] of water with an addition of as little as one-half to 5 p.p.m. of this hexametaphosphate, resulting in prevention of the afterprecipitation of calcium carbonate from softening operations, which would cause scale formation in pipes with consequent reduction in fluid flow and in heat transfer. This is important in domestic hot-water heaters, in water pipes, heat exchangers, and also in washing and laundering. The addition of the sodium hexametaphosphate also reduces corrosion particularly in nondeaerated waters.

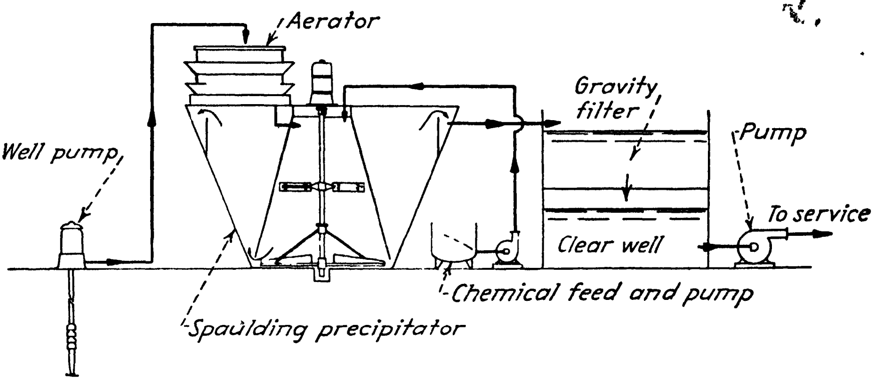

FIG. 4.—Municipal cold lime water softener and iron removal plant. (*Courtesy of The Permutit Company.*)

Silica Removal.—Dissolved silica is removed by none of the usual water-softening treatments. Silica may be a very objectionable impurity in feed water for high-pressure boilers as it can form a tenacious scale. It can be removed by absorption by ferric hydroxide, precipitated from ferric sulfate and lime. However, the absorption by magnesia or magnesium hydroxide[3] seems to be favored as having higher capacity and as not increasing the dissolved solids. This may be carried out with other conditioning steps such as removal of turbidity or lime-soda softening. Many times the source of the silica in the water is the use of sand filters for hot alkaline waters. This silica trouble may be eliminated by the use of calcite, magnetite, or anthracite coal as filter media.

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[1] The formula is sometimes given as $NaPO_3$ which is also called sodium phosphate glass or Calgon. See Chap. XVIII, under Sodium Phosphates.

[2] HATCH and RICE, Surface-active Properties of Hexametaphosphate, *Ind. Eng. Chem.*, **31**, 51 (1939); Corrosion Control with Threshold Treatment, *Ind. Eng. Chem.*, **32**, 1572 (1940); CERNA, Industrial Water Conditioning Processes, *J. Chem. Ed.*, **20**, 194, (1943); SCHWARTZ and MUNTER, Phosphates in Water Conditioning, *Ind. Eng. Chem.*, **34**, 32 (1942).

[3] TIGER, Silica Removal by an Improved Magnesia Process, *Trans. Am. Soc.*

Deaeration.—The removal of oxygen dissolved in water is often necessary to condition the water properly for industrial purposes, although this is unnecessary for municipal waters. Dissolved oxygen hastens corrosion by a number of reactions,[1] depending on conditions. The following is a typical presentation of an important phase of iron water corrosion accelerated by oxygen in alkaline or neutral conditions. Iron in contact with water exerts a certain solution pressure and sets up the oxidation or anodic half reaction:

$$\mathrm{Fe}(s) \rightarrow \mathrm{Fe}^{++}(aq) + 2e$$

This would cease after a certain potential was reached. However, oxygen can react with water to give OH ions at cathode areas:

$$\mathrm{O_2}(g) + 2\mathrm{H_2O}(l) + 4e \rightarrow 4\mathrm{OH}^-(aq)$$

The Fe^{++} and the OH^- ions would react and the electrons would neutralize by flow of current between the adjacent anode and cathode areas:

$$\mathrm{Fe}^{++}(aq) + 2\mathrm{OH}^-(aq) \rightarrow \mathrm{Fe(OH)_2}(s)$$

The initial reactions would then proceed further. This electrochemical corrosion can be summarized:

$$2\mathrm{Fe}(s) + \mathrm{O_2}(g) + 2\mathrm{H_2O}(l) \rightarrow 2\mathrm{Fe(OH)_2}(s)$$

Naturally air and water can change the ferrous into the ferric hydroxide. Anything that stops the foregoing sequences will stop the corrosion. This may be by the removal of the dissolved oxygen, by electrode polarization, by organic inhibitors, or by protective salts. Such protective salts would be chromates, silicates, phosphates, or alkalies which probably act as anodic inhibitors by forming a film over the anodic or active areas and thus interrupting the electrochemical sequences.

Water ordinarily saturated with air at 50°F. contains about 8 cc. oxygen per liter. Oxygen is removed by spraying or by cascading the

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Mech. Engrs., **54**, 1, 49–63 (1942); ANON., "Water Conditioning Handbook," Chap. 17, Permutit Co., New York, 1943.

[1] An excellent summary with references to the various phases of the corrosion of metals, largely based on this electrochemical mechanism, is presented by J. C. Warren in Chap. 9 of Leighou, "Chemistry of Engineering Materials," 4th ed., McGraw-Hill Book Company, Inc., New York, 1942.

water down over a series of trays contained in a tank. During the downward flow the water is scrubbed by uprising steam. An open feed-water heater of the spray type will usually lower the dissolved oxygen content to below 0.3 cc. per liter. Scrubbing devices will remove even this small amount, or it can be chemically combined using a scavenger like sodium sulfite:

$$O_2 + 2Na_2SO_3 \rightarrow 2Na_2SO_4$$

Such complete deoxygenation is necessary to avoid corrosion in the modern high-temperature high-pressure boiler.

Water Purification.—This usually signifies the removal of organic material and harmful microorganisms from municipal supplies. Coagulation and filtration through sand or hard coal and oxidation by aeration are usually sufficient to remove organic matter. This treatment also removes some of the microorganisms. As a further decrease is usually considered necessary in order to produce safe or potable water, treatment with chlorine is indicated. Large quantities of it are consumed in this manner to protect the health of the nation. The more powerful chloramine is also employed, and this is made in the water by feeding ammonia into the chlorinated water:

$$2NH_3 + Cl_2 \rightarrow NH_2Cl + NH_4Cl$$

This produces a better tasting water in certain instances. Chlorine is also used in water cooling to prevent the growth of organisms on the condenser interfaces with consequent increase therein in fouling factor in the heat-transfer coefficient.

Municipal Water Conditioning.—Treatment of municipal water supplies is usually necessary to produce potable and safe water.[1] Prior to widespread municipal treatment, epidemics particularly of typhoid fever were caused by contaminated water. The requisites of a safe municipal water supply are freedom from pathogenic microorganisms and freedom from suspended solids. It is also desirable, but not necessary, that the water be soft.

Figures 4 and 5 show a flow sheet for a municipal water-treating plant in which both purification and softening are carried out. The raw water is aerated to remove iron, odor, and taste, partly softened with lime, the precipitate coagulated and filtered. Chlorine may be added to destroy pathogenic microorganisms, and activated carbon[2] may be employed to remove odors and to improve flavor.

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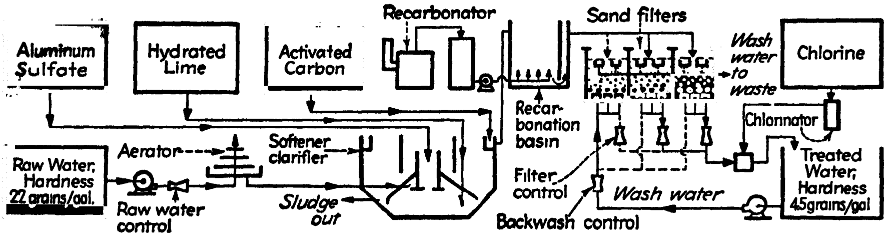
[1] BAYLIS, Assuring Quality in Public Water Supply, *Chem. & Met. Eng.*, **38**, 516–519 (1931).

[2] See Chap. IX; also PERRY, *op. cit.*, pp. 306–309.

Few municipalities have adopted softening as part of their water treatment because the public as yet does not realize the economic advantages of this process. The savings in soap alone are sufficient to more than pay for the cost of municipal softening. The many other advantages of soft water are, therefore, essentially free to the user.[1]

Industrial Water Conditioning.—The necessary quality of water for industrial purposes depends upon the special use to which it is to be put. In most cases hard waters cannot be utilized without treatment. Many process industries employ several kinds of water, each of which serves a particular demand and is previously treated specially for this purpose.



Raw water (22 grains)	750,000 gal.	Chlorine	50 lb.±	To produce 725,000 gal.± per day of 4.5 grain water
Hydrated lime	2,145 lb.±	Electricity	75 kw.-hr.±	
Aluminum sulfate	110 lb.±	Direct labor	24 man-hr.±	
Activated carbon	5 lb.±		–	

FIG. 5.—Municipal water treatment flow diagram. (*Courtesy of Infilco, Inc.*)

One of the most important industrial applications of water is for boiler feed. Untreated water, even if reasonably low in hardness, is usually not completely adapted to that use. It is, therefore, common practice to soften all water for use in boilers. Among the damages that untreated feed water may cause are rapid corrosion of boiler plates, tubes, and fittings, development of leaks caused by unequal expansion and contraction arising from overheating due to deposition of heat-insulating scale, bulging of tubes, loss of heat, and complete clogging of tubes due to scale deposits.[2]

The common processes for treating boiler feed water are the hot lime soda, hydrogen cation exchanger, and sodium zeolite depending upon the analysis of the raw water and the conditions at the plant. The feeding of water softened by these methods does not necessarily ensure that the boilers will be free from scale as the returns or condensates may become contaminated. It is, therefore, sound practice to employ also the trisodium phosphate treatment to precipitate any contaminating material that may get into the water. Deaeration to remove both oxygen and carbon dioxide are likewise necessary to decrease the corrosive action of the water.

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[1] OLSON, *op. cit.*, p. 607.

[2] PYBUS, Boiler Feed-water Treatment with Special Reference to Corrosion, *Gas World*, **98**, 9 (1933).

The quality of the water required for various operations in the process industries varies widely. Untreated water can be utilized satisfactorily for many purposes, especially if it is not too hard. Many processes, however, require very soft water. The textile industry must have softened water to ensure level dyeing. Other industries require, or find it advantageous to use, demineralized or distilled water. The ion-exchange process has reduced the cost of this pure water and has been installed in some process industries. Among the recent applications of this process are in mirror silvering, certain cellulose industries, plastics manufacturing, fine chemical and drug manufacturing, and synthetic rubber preparation.[1] Analytical and research laboratories have long used distilled water. The removal of inorganic salts frequently aids the recovery of dissolved organic materials. This has been applied to sugar sirups,[2] to gelatin, and to some other solutions.

SEWAGE AND INDUSTRIAL WASTE-WATER TREATMENT

Municipal Waste Waters.—Efficient *sewage disposal* is important to the health of any community. The easy method of disposal is by dilution, the waste being dumped into an available body of water such as a river or lake where the already present oxygen would in time destroy the organic sewage. This was the first method employed and is still used by many cities. However, public condemnation of this even temporary pollution of streams and lakes has led to the development of methods of treating the sewage so that it is no longer objectionable.

The present procedures may be divided into three main classes: mechanical treatments, chemical treatments, and activated sludge processes. Each of these classes entails the separation of the solids from the liquid followed by treatment of the two parts separately.

The impurity in a particular sewage or, in other words, the amount of treatment required is usually measured on one of two bases: (1) The amount of suspended solids, needs no explanation. (2) The biological oxygen demand (B.O.D.), measures the amount of impurities by the amount of oxygen required to oxidize it.

Mechanical methods of removing solids are passing the sewage through screens, or filters, grit chambers (shallow rectangular tanks in which the velocity of flow is checked so as to cause the grit to settle out, carrying some of the organic material with it), sedimentation basins, and trickling filters. In some installations, the various methods are employed in series. The procedures of Fig. 6 depict mechanical screening, followed by activated sludge treatment, thickening, and filtering.[1]

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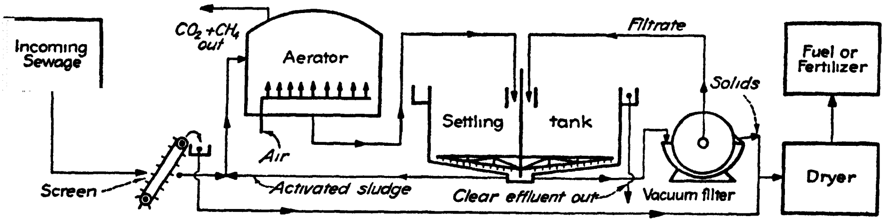
[1] TIGER and SUSSMAN, *op. cit.*

[2] RAWLINGS and SHAFOR, Ionic Exchangers, Their Application in Cane and Beet Sugar Juice Purification, *Sugar*, **37**, No. 1, 26 (1942); WEITZ, Juice Purification by Ion Exchange as Applied to the Arabella Sugar Co., *Sugar*, **38**, No. 1, 26 (1943); MYERS, Synthetic Ion Exchange Resins, *Chem. Industries*, **51**, 712 (1943). See also NORDELL, Demineralizing Industrial Water and Process Liquors, *Chem. & Met. Eng.*, **50**, No. 10, 112 (1943).

Chemical treatment precipitates the solids by coagulation. The coagulated materials are removed by sedimentation or filtration. Coagulants of importance are ferric sulfate or chloride or aluminum sulfate with lime.

Activated sludge provides one of the most effective methods for removing both suspended and dissolved substances from sewage. The activated sludge contains aerobic microorganisms which digest the raw sewage. Some activated sludge from the previous run is introduced into the raw sewage and air blown in, not in excess but only in the amount needed (see Fig. 6).



Average technical data Air required 0.35 to 1.94 cu ft per gal sewage, detention in aeration tank, 4-6 hrs, detention in settling tank, 1½-2 hr, sludge return to aerator, 10-50 percent of total

FIG 6 —Activated sludge sewage disposal.

The disposal of the solids removed by any of these processes depends upon the local conditions. In some cases they are buried, burned, or sold as fertilizer material after filtering and drying.[2] The liquids remaining after the removal of the solids are usually chlorinated to destroy harmful microorganisms and then discharged into near-by streams.

Industrial Waste Waters.—The disposal of industrial waste waters presents a much more difficult problem than that of sewage. Each waste water must be treated according to its specific chemical nature. Waste pickling liquor containing ferrous sulfate or ferrous chloride, and waste sulfite liquor carrying large amounts of organic matter in the form of sulfonic acids, have become sources of very serious contamination of streams in many sections of our country. It has been estimated that the iron and steel plants of the United States produce 500,000,000 to 800,000,000 gal. of waste pickle liquors per year. These liquors average in composition: H_2SO_4, 5 per cent; $FeSO_4$, 15 per cent; H_2O, 80 per cent. In addition to these two wastes, there are many others such as those flowing from dye works and leather tanneries. In handling such wastes, the aim is, of course, to treat them so as to obtain something of value from the disposal operations or at least to conduct them at minimum expense.

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[1] PERRY, *op. cit.*, p. 1687, presents sewage dewatering after sludge conditioning. Such cake moistures are high (65 to 85 per cent water). *Cf.* p. 1849 for centrifugating of sewage sludges.

[2] ANON., Flash Drying of Sludge, *Chem. & Met Eng.*, **48**, No. 1, 108 (1941). This article gives a detailed pictured flow sheet for disposal of activated sludge from Chicago's large Southwest Works treating 400,000,000 gal. daily.

Two solutions have been found for the pickling liquor problem. One plant of the American Rolling Mill Company operates a process for making ferrous sulfate. The Ferron process consists in precipitation with lime to give a slurry which is filtered, dried, and used as a building and insulating material.[1]

Many uses have been found for small amounts of the waste sulfite liquors after they have been concentrated by evaporation. The adhesive properties have been employed in briquetting powdered fuels, in core binders, and in linoleum cements. Other applications are as a tanning agent and as an ore flotation agent. The newest treatment process is that used by the Marathon Paper Mills, wherein the waste liquor is treated with lime in three stages to precipitate calcium lignin sulfonates. The lignin derivative produced finds its greatest consumption in plastics and to some extent for the production of vanillin.

The Dow Chemical Company has a variety of waste liquors which are handled in well-designed units. The waste brines are stored in ponds and released when the flow in a near-by river is high.[2] Taste- and odor-producing wastes such as tars and cracking oils are allowed to settle out and accumulate in a pond, with the clean water being returned to the plant as a cooling and scrubbing liquid. Phenolic wastes are treated by bacterial action on trickle filters. Sedimentation basins remove solids from the wastes, while gases are treated by Cottrell precipitators and scrubbing towers.

Calco Chemical also has a large variety of effluents and a well-designed $325,000 plant for treating them.[3] The first step consists in special treatments for the most troublesome wastes at their source. All wastes are then mixed thoroughly so that acids may neutralize bases and the various colors counteract each other. Further steps include neutralization of residual acidity, final settling, bleaching, and aeration.

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[1] Howe and Van Antwerpen, A Symposium on Industrial Wastes, *Ind. Eng. Chem.*, **31**, 1323 (1939); Hodge, Wastes Problems of the Iron and Steel Industries, *Ind. Eng. Chem.*, **31**, 1364 (1939).

[2] Marlow, Waste Problems of a Chemical Plant, *Ind. Eng. Chem.*, **31**, 1346 (1939).

[3] Mensing, *et al.*, Calco's Waste Treatment Plant, *Chem. & Met. Eng.*, **48**, 84 (1941).

Problems

1. A water contains the following metals, expressed in milligrams per liter: Ca^{++}, 30; Mg^{++}, 10; Fe^{++}, 0.5.

a. Calculate the total hardness expressed in milligrams of equivalent $CaCO_3$ per liter.

b. Assuming that 95 per cent CaO costs $11 per ton, calculate the cost of softening 1,000 gal. of this water.

2. A water has the following analysis expressed in grains per gallon (7,000 grains per lb.): $Ca(HCO_3)_2$, 7.00; $Mg(HCO_3)_2$, 2.92, $MgCO_3$, 1.00; $CaSO_4$, 1.36; $MgSO_4$, 2.16. Assuming 100 per cent CaO, Na_2CO_3, and NaCl cost $11, $20, and $4.50 per ton, respectively, calculate

a. The cost of softening 1,000,000 gal. a day by the lime-soda process.

b. The cost of salt per day for regeneration of zeolite if 0.5 lb. of salt is required for each 1,000 grains of hardness (as $CaCO_3$) removed from the water.

3. A water has the following ions present, p.p.m.: Ca^{++}, 75; Mg^{++}, 10; HCO_3^-, 190; CO_2, 11. If lime costs 68 cents and Na_2CO_3 costs $1.30 per 100 lb. what is the total cost for softening 800,000 cu. ft. of water?

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CHAPTER V

FUELS, POWER, AND AIR CONDITIONING

As a rule, a chemical engineer is not enough of a specialist to be capable of adequately designing plants for the production of power, for refrigeration, or for conditioning air. However, chemical processes are such large users of heat, power, cold, and air, that he should be familiar with the broad technical aspects of the production of these essential tools. He should also be prepared to work with power and refrigeration engineers in the proper coordination of the production of heat, power, and cold and their use in chemical processes in order to attain the cheapest manufacturing costs. Frequently the cost of power, particularly if it is going to be used electrochemically, is the deciding

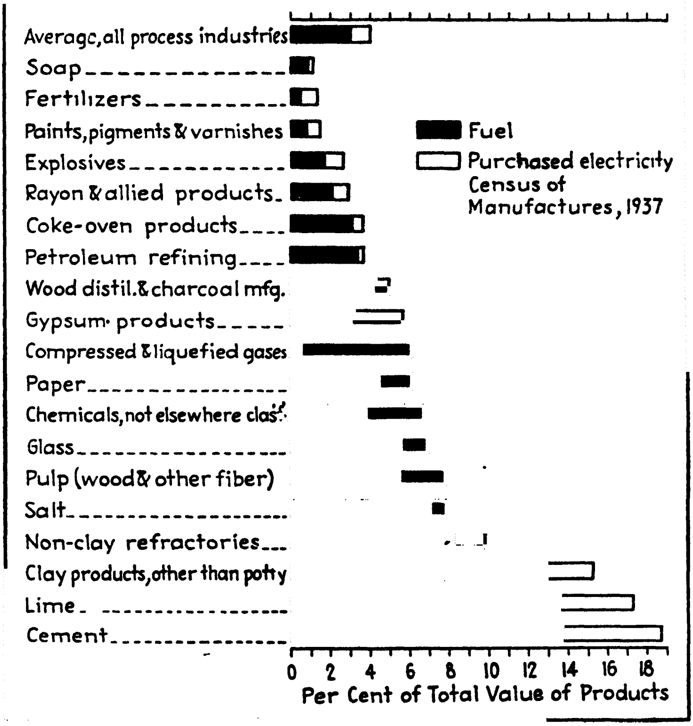

FIG. 1.—Energy consumption in process industries as represented by fuel and purchased electricity. (*Courtesy of Chem. & Met. Eng.*)

factor in the location of a given factory. Those process industries under the direction of chemical engineers are in most instances outstanding consumers of steam for evaporation, heating, and drying. Consequently these industries need large quantities of steam usually in the form of low-pressure or exhaust steam from turbines or steam engines. Occasionally however, certain exothermic reactions, as in the contact sulfuric acid process, can be employed to generate steam for use.

If only electricity is desired from a steam power plant, naturally the turbines are run condensing; if, on the other hand as in the chemical process industries, both steam and power are needed, it is economical to take the high-pressure steam directly from the boilers through non-condensing turbines obtaining exhaust steam from these prime movers to supply the heat necessary for drying, evaporation, and endothermic chemical reactions throughout the plant. Figure 1 presents, by industry, the fuel burned for power and heat in comparison with purchased electricity.

TABLE 1.—COMPARISON OF ENERGY FROM STEAM BY EXPANSION FOR POWER AND BY CONDENSATION FOR HEAT[a]

Condition 1		Work operation, B.t.u. per lb. by expansion from condition 1 to saturated steam at 15 lb. gage	Heat operation, B.t.u. per lb. by condensation of steam exhausted from work operation, to water at 212°F.
Gage pressure, lb. per sq. in.	Superheat, degrees F.		
300	348	240	984
200	279	192	984
150	235	161	984
100	177	121	984
50	95	65	984

NOTE: Superheat is necessary to prevent erosion of turbine blades by moisture in the steam. The amount is figured to furnish saturated steam after expansion to 15 lb. gage.

[a] Data calculated from Keenan and Keyes, "Thermodynamic Properties of Steam," John Wiley & Sons, Inc., New York, 1936.

Heat Balance.—The economics of the dual use of heat and power concerns the desirability of coordinating the generation of steam for power and for process heat so that the power needed is obtained as a by-product of the process steam demand. The first step in balancing these two energy demands should be a careful, accurate survey[1] of the heat and power requirements of the various processes.

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[1] SWAIN, By-product Power in Process Industries, *Chem. & Met. Eng.*, **48**, No. 3, 94 (1941), several different balances of steam and power are here described and diagramed; STUDLEY, Heat and Power Balance in Chemical Plants, *Chem. & Met. Eng.*, **41**, 464 (1934); PERRY, *op. cit.*, pp. 2471–2477, presenting various diagrammatic and quantitative steam-power arrangements.

Since superheat usually retards the rate of heat transfer for process operations, the condition of the steam at the turbine exhaust or at the bleeding point should be such that it will have sufficient superheat to overcome transmission losses but yet have little or no superheat when it reaches the point of use. This will result in the full utilization of the latent heat of steam for heating purposes.

TABLE 2.—SOURCES OF INDUSTRIAL ENERGY[a]

	All manufacturing industries	Chemicals and allied products	Chemicals n.e.c.[b]
Coal, short tons:			
Anthracite	5,015,857	641,495	332,124
Bituminous	137,771,432	9,658,592	4,743,352
Coke, short tons	35,115,357	438,718	350,898
Fuel oil, bbl	133,773,524	11,492,567	6,574,231
Gas, million cu. ft	2,195,094	320,102	51,419
Electricity,[c] 1,000 kw.-hr	45,040,074		
Electricity, cost	$465,406,864	$35,783,324	$16,560,926
Establishments	184,230	9,203	543
Wage earners	7,886,567	287,136	60,268
Value of products	$56,843,024,800	$3,733,657,723	$839,750,366

[a] Data compiled from U.S. Census, 1939.

[b] n.e.c. = not elsewhere classified.

[c] Purchased electric energy only; does not include electrical energy generated in manufacturing plants.

The fundamental importance of this principle of coordination of the steam for power and the steam for process heating can be seen by inspection of Table 1 which gives the B.t.u. converted to power by expansion of steam at various pressures and superheat to saturated steam at 15 lb. gage as contrasted with the B.t.u. supplied by the condensation of this exhaust steam. As process steam must be supplied for the heat-transfer operations, it may be seen from Table 1 that the obtaining of what power is available by expansion is probably the most economical power a plant can get. Consequently the ideal plant would expand all of its steam through turbines for power and then lead the exhaust steam into the factory for the various heat-transfer operations. When there is no contamination of this process steam, the water from the condensation should be brought back for the boiler feed make-up water. All chemical industries should be studied for this dual use of steam. Those pertaining to manufacture of sugar (Chap. XXX), caustic soda (Chap. XV), salt (Chap. XIV), and fermentation (Chap. XXXI) have applied this dual energy balance very profitably.

To balance the power required as made by expansion of steam, with the process demands for steam exhausted from the steam engine or turbine so that there is no excess of either, should be the aim of the engineers in charge of any plant. This ideal can frequently be realized in the chemical process industries. Many studies[1] of different arrangements have been made but all point to the lowered cost of electrical energy and of steam by this dual use of the primary steam.

FUELS

Fuels can be divided into three classes: solid, liquid, and gaseous. To these as an energy source should be added water power. Figure 2 depicts the trends in the use of these four sources of energy. The actual and comparative cost of the different energy supplies varies with the different parts of the country. With coal at $2 or $5 per ton, 1,000,000 B.t.u. will cost in fuel 7 cents or 17 cents, respectively; with fuel oil at 5 cents per gal., these B.t.u. will cost 35 cents. For city gas at 50 cents per 1,000 cu. ft., these same B.t.u. will amount to 84 cents, or for electricity at 5 cents per kw.-hr., $1.47.[2] Coal is the most important fuel used for power purposes but there is a trend to use a cleaner fuel such as fuel oil or gas and to develop better methods of coal combustion which result in less contamination of the atmosphere. This is especially true in large towns and cities.

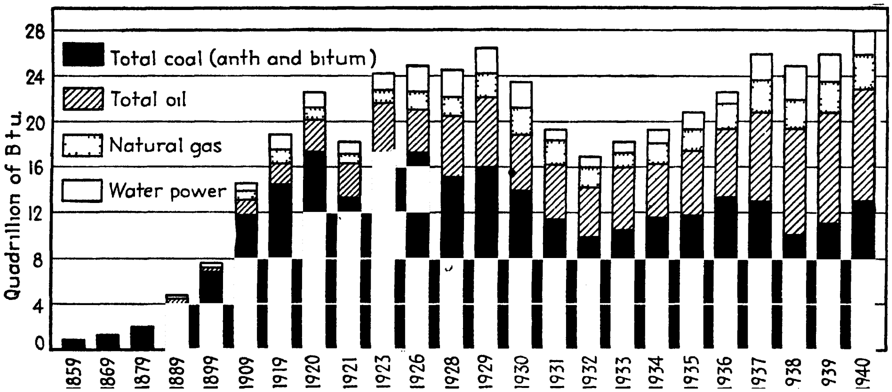

Fig. 2.—Trends in fuel and energy supply in the United States. (*Courtesy of Chem. & Met. Eng.*, **44**, 537 (1937) *and Statistical Abstract of the United States*)

Liquid fuels are derived mainly from petroleum and follow coal in importance as a source of heat for power generation. Petroleum products also furnish almost all of the energy for the numerous internal-combustion engines of this country.

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[1] Various authors, Modern Aspects of the Use of Steam in Chemical Engineering Industries, *Chem. & Met. Eng.*, **34**, 529–580 (1927).

[2] Perry, *op. cit.*, p. 2801, tabulates further fuel costs per 1,000,000 B.t.u.

The fuel gases are either natural or artificial and are presented in Chap. VII. These gases, although made primarily as a source for heat, are being consumed in increasing amounts as basic raw materials for chemical manufacture.

Solid Fuels.—*Coal* is the most important of the solid fuels with an annual consumption around 500,000,000 tons.[1] No entirely satisfactory scheme has been worked out for classifying coals but a generally accepted method divides coal into the following classes: anthracite, bituminous, subbituminous, and lignite, with further subclassification into groups.[2] The bituminous coals are used most extensively for power purposes. Anthracite is a valuable domestic fuel because of its clean-burning characteristics.

Since coal compositions vary so widely, a fuel analysis[3] is necessary from both the purchasing and the combustion viewpoint. The *proximate analysis* determines the percentages of moisture, volatile matter, ash, and fixed carbon (by difference) in the coal. The sulfur content is determined also and *reported with the proximate analysis but it is not considered a part of it.* The procedures for determining the proximate analysis have been standardized by the A.S.T.M.[4]

The *ultimate analysis* gives the percentages of carbon, hydrogen, sulfur, oxygen, nitrogen, and ash (by difference) in the coal. This analysis can be used for boiler test calculations and for determining the approximate heating value of the fuel. If this analysis is available, the formula of Dulong may be used with an accuracy of within 2 or 3 per cent.

$$\text{B.t.u. per lb.} = 14{,}544 \times \text{fraction C} + 62{,}100 \times (\text{fraction H} - \tfrac{1}{8}\,\text{fraction O}) + 4{,}050 \times \text{fraction S}$$

The B.t.u. per pound on ash- and moisture-free basis varies from 14,070 for Pennsylvania anthracite to 15,670 for West Virginia semibituminous. A more accurate method of determining the heat of combustion of the fuel consists of actually burning the coal in an oxygen atmosphere under pressure in a bomb calorimeter and measuring the heat evolved.

The storage of coal is an important problem in industrial practice. Underwater storage is frequently employed at present to avoid too rapid weathering and spontaneous combustion. The presence of some moisture and pyrite, or any easily oxidizable material, in bituminous coal, may cause coal to ignite; the rise to 50°C. is slow but, from there to the ignition point the rise may be rapid if conditions for the dissipation of heat are poor.

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[1] See *ibid.*, p. 2326, for details.

[2] *Ibid.*, pp. 2327, 2328.

[3] *Ibid.*, pp. 2329–2336, for tabulations of analyses and properties.

[4] *Ibid.*, p. 2331.

Powdered coal has been used to an increasingly large extent in recent years in power-plant installations because of the high thermal efficiency with which it can be burned, the low cost of operation and maintenance, and its excellent flexibility. All these factors more than balance the increased cost of preparing the fuel.[1] One serious disadvantage in burning powdered coal is the "fly ash" which leaves the boiler carried along with the waste gases. This is a very fine ash which settles over surrounding territory as a nuisance. It can be removed from the flue gases by a Cottrell precipitator,[2] but the problem of disposal still remains. It has been made into bricks, building blocks, and even roofing tile, after compression, by reaction with slaked lime under steam pressure.[3] As only slaked lime and water are needed in addition to the fly ash, the development of this process may encourage the further employment of powdered coal as a fuel.

Coke is a fine fuel but it is too expensive at present for industrial use except in special cases as in blast-furnace operation, where it is a chemical raw material as well as a fuel. Coke is a valuable fuel for domestic heating plants. As the by-products of coal distillation increase in value with a decrease in other hydrocarbons such as from petroleum, the increased use of coke as a fuel is indicated. Other solid fuels[4] such as coke "breeze," wood, sawdust, bagasse, and tanbark are used where they are available cheaply or where they are produced as by-products.

Liquid Fuels.—*Fuel oil* is the only important commercial liquid fuel used for power purposes. It is the portion of the crude oil that cannot be economically converted by the refiner to the higher priced products such as gasoline. It consists of a mixture of the liquid residues from the cracking processes with fractions of a suitable boiling point obtained from the distillation of crude oil. The fuel oil[5] is classified according to its properties such as the flash point, pour point, percentage of water and sediment, carbon residue, ash, distillation temperature, and viscosity. All of these are determined by tests that have been standardized by the A.S.T.M. The flash point is relatively unimportant for determining the behavior of the fuel in the burner, but it has some importance in the storage of the oil since storage tanks should be kept well below this temperature. Oil-burning equipment usually shows a higher thermal efficiency (75 per cent) than coal-burning boilers, and labor costs are usually less. However, the latent heat loss of steam produced by the combustion of the hydrogen of the fuel oil is about two times greater than such losses from bituminous coal.

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[1] *Ibid.*, pp. 2347–2349 lists such costs.

[2] *Ibid.*, pp. 1807–1879, but particularly Table 10 on p. 1877.

[3] Rostone Corp. of Lafayette, Ind.

[4] PERRY, *op. cit.*, p. 2340.

[5] *Ibid.*, pp. 2343–2357 gives specifications, costs vs. coal, heats of combustion, chemical constituents, and oil-burning equipment.

TABLE 3.—SUMMARY OF INFORMATION ON STOKERS[a]

	Chain grates	Overfeed stokers	Underfeed stokers
Description	Fuel is carried horizontally into furnace on a continuous web which is cooled coming out through the ash pit.	Grate extends from hopper into furnace at a rather steep incline with coal entering only during a rocking movement imparted to grate bars.	Raw coal is pushed up through the fuel bed and coked. Clinker falls off to side. Volatiles distilled off are burned in an oxidizing atmosphere.
Fuel used	1. Coke breeze, steam sizes of anthracite or 2. High volatile Middle Western coals. In general any noncoking, clinker coal may be used.	All coals can be used. Good all-round stoker. Is used mainly on Middle Western fuels. Coking coals can be used. Will burn refuse fuels.	High-volatile coals, coking coals, and slack or fines may be burned. Ash must not be easily fusible.
Draft	Natural: 0.25 to 0.60 in. water. Forced: 1 to 2 in. water pressure with coke or somewhat higher for Illinois and similar coals.	Natural: 0.25 to 0.6 in. water. Forced: 1 to 3 in. water pressure.	All forced draft. Normal: 2 to 4 in. water pressure in wind box, occasionally higher.
Rate of combustion, lb. per sq. ft. per hr.	Average: 30 to 35. Maximum: 45 to 60.	Average: 25 to 35. Maximum: 40 to 50.	Average: 30 to 40.
Means of regulation	1. Height of coal grate. 2. Speed of grate. 3. Amount and distribution of air.	1. Rate of plunger feeder. 2. Rate of ash removal. 3. Amount and distribution of air.	1. Rate of feed. 2. Amount and distribution of blast.
Miscellaneous	Watch for live coals going over end of grate.	Fireman needed for ash removal at times and for cleaning of fire.	Air is admitted to burn out cinder. Fuel bed from 12 to 24 in. deep.

[a] Shortened from Perry, *op. cit.*, p. 2336; see diagram, p. 2337.

Other liquid fuels include coal tar, tar oil, kerosene, benzol, and alcohol, which are consumed to a relatively smaller extent than is fuel oil. Gasoline is consumed mainly in internal-combustion engines.

Gaseous Fuels.—Gas is burned as a source of heat in domestic installations and occasionally in industry, especially where it is obtained as a by-product. Blast-furnace gas resulting from the smelting of iron is an outstanding example of where a by-product gas is employed for heating the blast stoves, with the remainder burned under boilers or for heating coke ovens. The other gases that may be used for power generation are natural gas, when available, and the manufactured gases such as coke-oven gas, producer gas, and water gas. These are discussed more fully in Chap. VII where a tabulation is given of B.t.u. values and other properties.

Combustion.—Most modern industrial plants burn coal either on mechanically operated grates and stokers or in the powdered form. Table 3 gives a summary of the information on stokers. These present-day procedures enable the ratio of air to the fuel to be properly controlled, thus ensuring efficient combustion and reducing heat losses through stack and ash.

When fuel oil is burned, it is frequently necessary to provide heaters to lower the viscosity of the oil sufficiently for the proper burner operation.[1] The burners consist of an atomizer which mixes the fuel with the primary air. The secondary air is usually supplied through the base of the furnace.

For gaseous fuels the burner consists of a gas orifice, an injecting tube in which the air is entrained and mixed with the gas, and ports from which the air-gas mixture is discharged into the combustion zone.

The flue-gas analysis is valuable in controlling the combustion since the proportions of CO_2, CO, and O_2 in the flue gas will indicate incomplete combustion or excess air. Frequently power-house employees are paid a bonus for satisfactory combustion as indicated by flue-gas analyses. The chemical engineer has been particularly concerned with efficient combustion as one of his contributions to efficient plant operation.[2]

POWER GENERATION

Near the end of the seventeenth century the first successful attempt to generate steam under pressure in an enclosed vessel was made. Since then the use of steam has increased to such an extent that today steam furnishes about 75 per cent of the total power developed in this country.

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[1] *Ibid.*, pp. 2352–2387.

[2] See particularly the combustion chapter, pp. 173*ff.*, in Walker, Lewis, McAdams, and Gilliland "Principles of Chemical Engineering," 3d ed., McGraw-Hill Book Company, Inc., New York, 1937.

The most recent developments have been toward improvements in boiler construction with the aim of producing higher pressure steam, even up to 1,200 lb. in central power stations. Such high pressures[1] increase the over-all efficiency in the production of electric power. The limiting factor is the failure of materials at the high temperatures and pressures involved.

There are two main types of boilers: the fire tube (Fig. 3) and the water tube (Fig. 4). The *fire-tube boiler* is usually of small and medium capacity and is designed for the generation of steam of moderate pressure. In this type the fire passes through the tubes. Fire-tube boilers have a low first cost and a relatively large reservoir of hot water. This is of particular advantage in small chemical plants where there may be a sudden demand on the steam plant. Locomotive boilers are also of this type.

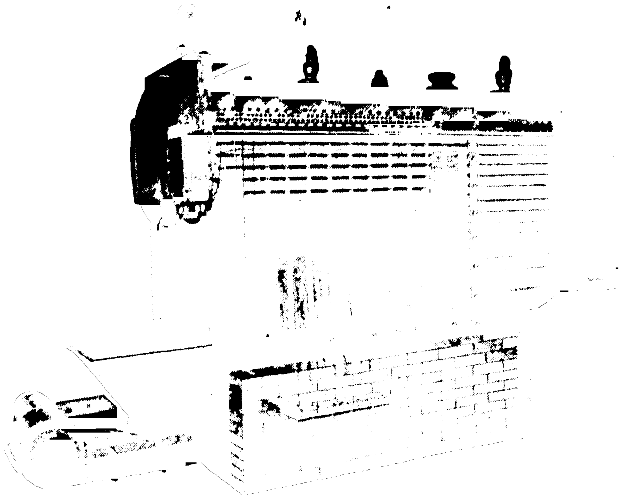

Fig. 3.– Longitudinal section of a fire-tube boiler of the "economic" design arranged for stoker firing. This type of boiler is self-contained and can be used for coal, oil, or gas firing. (*Courtesy of Erie City Iron Works.*)

Water-tube boilers are used almost exclusively in stationary installations where service demands a large amount of evaporation at pressures above 150 lb. per sq. in. The water is in the tubes and can be converted to steam more quickly than with the fire-tube type ("quicker steaming"). High efficiencies are obtained by this type. The positions of the drums and tubes, the slope, and the shapes of the tubes are the distinguishing characteristics among different makes of these boilers.

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[1] Perry, *op. cit.*, p. 2432. The entire section on Power Generation, pp. 2432–2493, should be consulted. Horsepower and boiler rating are presented on p. 2444.

Boiler feed water should be conditioned before introduction into the boilers (Chap. IV). Poor boiler water results in foaming, caustic embrittlement, corrosion, and scale formation with consequent loss in steam made and in efficiency. The higher the pressure, the more important is the use of properly conditioned water.

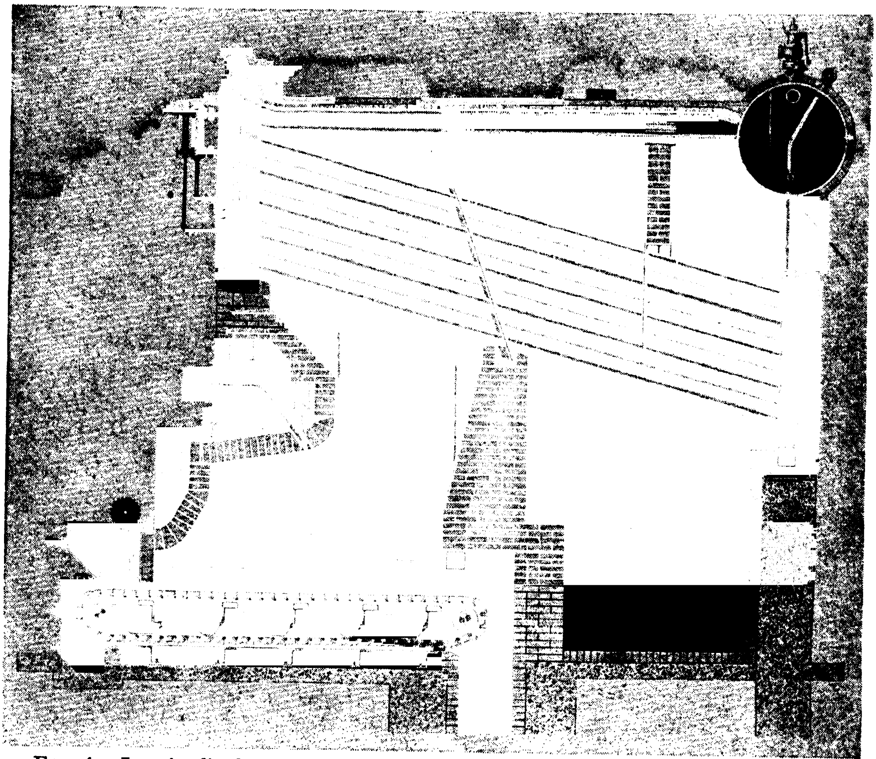

FIG. 4.—Longitudinal section of a water-tube boiler of Babcock and Wilcox design. Cross-drum boiler built with heating surface from 1,000 to 6,000 sq. ft. to provide steam up to 250 lb. pressure. (*Courtesy of The Babcock & Wilcox Company.*)

Electric Power from Steam.—Steam is often regarded as being raised solely for generation of power. However in the process industries, particularly in those pertaining to the making of chemicals, so much heat is obtained by condensation of steam, that the dual use of steam for power and for heat is of paramount importance. An economical engineer endeavors to coordinate and balance the two.

In these chemical processes, the object should be to expand the steam through the steam engine or turbine[1] and then employ the exhaust or lower pressure steam for heating purposes. In this procedure the prime movers are run noncondensing. For turbines, where dry steam is necessary to prevent blade erosion, the entering steam should be superheated and condensation prevented. The turbine is a particularly flexible prime mover for chemical plants as it can be designed not only to furnish low-pressure exhaust steam but, by bleeding off, to supply steam of higher pressures. This enables the primary steam to be efficiently raised at the modern high pressures, too high to be suitable for ordinary plant heating.

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[1] *Ibid.*, pp. 2455–2463; for electric generators see pp. 2705*ff.*

Hydroelectric Power.—Many of the chemical industries require large amounts of low-priced electric power for their operation. These companies usually locate near a hydroelectric plant where cheap power is available, especially to the large steady day-and-night consumer. Such industries are the electrochemical ones covered by Chap. XVI on the Electrolytic Industries and Chap. XVII on Electrothermal Industries. These hydroelectric plants are situated where there is a head of water available either from a waterfall or from a dam. This water is used to drive a water wheel[1] of some sort to which is attached either a direct- or alternating-current generator. The initial cost of a hydroelectric plant is much greater than of a corresponding steam power plant, but the running cost is much lower.

Heat Transmission Other Than by Steam.—Where indirect heating is necessary, some method other than steam should be used for temperatures above about 400 or 450°F., where the pressure of steam becomes too high for economical design of the plant. As steam owes its importance as a heating medium to its convenience and cleanliness, but particularly to its large heat of condensation, the use of superheated steam is not indicated as a heating medium except in rare cases. Hence, where the conditions lie outside the range of steam, the engineer[2] turns progressively, as the temperature rises, to

Direct firing, above 300°*F.*: low cost and convenience but fire hazard.

Indirect firing, above 300°*F.*: low operating cost but elaborate setting and fire hazard.

Direct gas heating, above 300°*F.*: moderate cost and excellent control but fire hazard.

Hot oil, 300 *to* 600°*F.*: good control but high first cost and oil carbonization.

Dowtherm, 300 *to* 700°*F.*: good control and moderate operating cost but higher first cost.

Mercury vapor, 600 *to* 1200°*F.*: good control and moderate operating cost but highest first cost.

Mixed salts, 250 *to* 900°*F.*: good control and good heat transfer at high temperature.

Electricity, above 300°*F.*: most accurate control but operating cost usually high.

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[1] *Ibid.*, p. 2469.

[2] A much more elaborate table accompanied by specific diagrams and descriptions is given by Perry, *op. cit.*, pp. 1578–1581.

Direct or indirect heating with coal or gas is frequently surprisingly efficient when the furnace is well designed; however the open flame may be a bad fire hazard. Under conditions where oil is not carbonized, this heat-transfer medium has been so widely employed that furnaces for heating the oil and equipment for the heat transfer are both available on the market as standardized and tested designs. Dowtherm[1] (diphenyl or diphenyl oxide or a eutectic mixture of the two) is stable at higher temperatures than oil and has the added advantage that it can be employed as a vapor where its latent heat of condensation can be used as well as its sensible heat. Mercury is very successful in controlling the heat of reaction in the Downs[2] reactor for vapor phase oxidation of naphthalene to phthalic anhydride. For years, mixtures of inorganic salts have been accepted as heat-transfer media, but it needed the modern large-scale demand for such salts to *remove* heat from petroleum cracking processes such as the Houdry catalytic one, to justify a careful study of the properties of the mixed salt[3] consisting of approximately 40 per cent $NaNO_2$, 7 per cent $NaNO_3$, and 53 per cent KNO_3. Strange to say, tests in the reference cited indicate no danger even if a stream of hot petroleum were injected into the molten nitrate-nitrite bath. Electricity in contact, immersion, or radiant heaters is a most convenient, accurate, safe, and efficient though generally costly heating medium.

REFRIGERATION

Refrigeration[4] is the process of producing cold, particularly referring to cooling below atmospheric temperature. It is a vital factor in many chemical processes where cold or the removal of heat is necessary for reaction control. Examples are the manufacture of azo dyes, separation of an easily freezing product from liquid isomers or impurities, and the food and beverage industries. Refrigeration operations involve a change of phase in a body so that it will be capable of abstracting heat, exemplified by the vaporization of liquid ammonia and the melting of ice.

Mechanical refrigeration can be divided into two general groups: the *compression system* and the *absorption system.*[5] Both systems cause the refrigerant to absorb heat at the low temperature by vaporization and to give up this heat at the higher temperature by condensation. The absorption system is used mainly in household units, but it finds economical industrial application where exhaust steam is available.

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[1] Heindel, Developments in Heat Transfer with Organic Compounds, *Chem. & Met. Eng.*, **41**, 308 (1934).

[2] U.S. Pat., Downs 1604739 of Oct. 26, 1926; Hulsart, Mercury Vapor As Applied to Process Industries, *Chem. & Met. Eng.*, **41**, 313 (1934); Craig and Anderson, "Steam Power and Internal Combustion Engines," p. 348, McGraw-Hill Book Company, Inc., New York, 1937.

[3] Kirst, Nagle, and Castner, New Heat Transfer Medium for High Temperature, *Trans. Am. Inst. Chem. Engrs.*, **36**, 371–390 (1940).

[4] Perry, *op. cit.*, pp. 2527–2638. This section has extensive diagrams and tables of thermodynamic properties.

[5] *Ibid.*, pp. 2527, 2529, 2540.

An ammonia refrigerating plant will give a typical illustration of the vapor-compression system and is depicted by Fig. 5. Here the vapor from the cold room is compressed and leaves with such enhanced pressure that the liquefaction temperature at this pressure is above that of the atmosphere or other coolant. From the compressor, the refrigerant goes to a liquefying condenser where the heat of condensation is removed by the atmosphere or cooling water. The now liquid refrigerant passes through an expansion valve which separates the high- from the low-pressure regions. The refrigerant in this low-pressure condition enters through the cold room where the heat of vaporization of the ammonia is abstracted from the surroundings. The cold room may not be a room at all but may consist of coils immersed in brine with the cold brine being then circulated to the points where refrigeration is necessary. The vapor then repeats this cycle with no loss of refrigerant except by leakage.

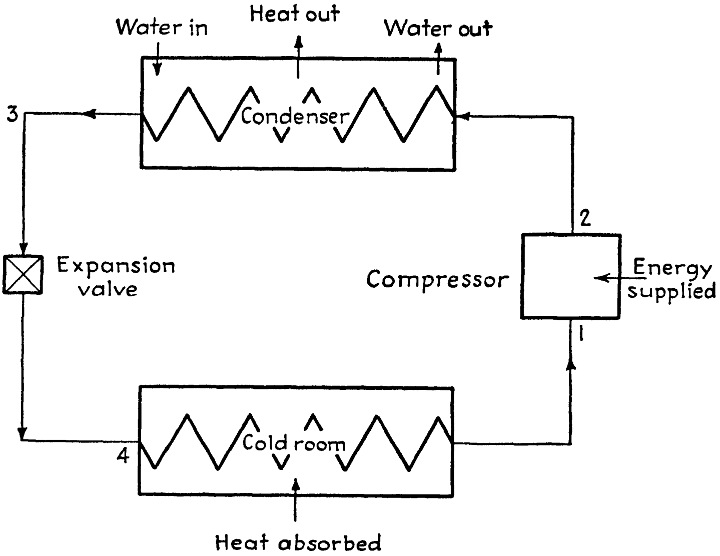

FIG. 5.—Compression system for refrigeration.

Besides the requirements dictated by the thermodynamics of refrigeration, a good refrigerant must also satisfy various economic and practical requirements. For example, a good refrigerant should be cheap, inert, and stable. It should have no corrosive tendencies, should be nontoxic and nonexplosive, and should have no properties injurious to goods and foods depending upon its application. Another important property should be ease of detection in case of leaks.

Ammonia is by far the most commonly employed refrigerant, especially in large industrial installations. Carbon dioxide is used to a great extent on shipboard where a nontoxic refrigerant is desired; it has recently been replaced by Freon on battleships. Sulfur dioxide has been employed extensively in household refrigerators. All three of these refrigerants have certain disadvantages which have stimulated search for better agents without their bad qualities. Freon, CCl_2F_2, is an outstanding development in this respect. It possesses the distinct advantage of being nonflammable, nontoxic, and noncorrosive to most metals. Table 4 summarizes the properties of the usual refrigerants.

TABLE 4.—PROPERTIES OF REFRIGERATING AGENTS[a]

Refrigerant	Boiling point at 760 mm., degrees F.	Critical temperature, degrees F.	Critical pressure, atmospheres	Latent heat at 760 mm., B.t.u. per lb.
Ammonia, NH_3	− 28	270.5	111.5	589
Carbon dioxide, CO_2	−108.8[b]	88.3	73.0	126[c]
Sulfur dioxide, SO_2	+ 14	315.3	77.7	167
Methyl chloride, CH_3Cl	− 11	298.9	65.8	184
Ethyl chloride, C_2H_5Cl	+ 55	369.3	52.0	168
Freon, CCl_2F_2	− 21	.....	.....	71.9
Propane, C_3H_8	− 44.4	206.6	42.0	159

[a] PERRY, *op. cit.*, pp. 474–476, 2550–2589.

[b] Sublimes.

[c] Latent heat at −20°F. and 220.6 lb. per sq. in. abs.

AIR CONDITIONING

The use of air conditioning in industrial plants has become more and more common in the past few years. Control of the temperature, humidity, and cleanliness of the air is very important in many chemical processes, particularly in artificial fiber and paper manufacture. Textile fibers are quite sensitive[1] to changing conditions of the air. The comfort of the worker is also important to efficient industrial organizations. This fact has led to the use of air conditioning in plants and offices where it is not essential for product quality.

Air-conditioning equipment consists of apparatus for the addition or removal of heat and moisture from the room being conditioned and automatic control for this apparatus so that the temperature and humidity can be conditioned within the desired limits. Humidification is usually done in an indirect humidifier in which water or steam is sprayed directly against the incoming air and the humidified air is then warmed by passage

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[1] *Ibid.*, pp. 1088–1091, presents tables showing the effect of changing humidity upon various products of chemical factories.

over tempering coils. For summer use the air is washed in a spray chamber and then cooled and dehumidified by passage over refrigerator coils.[1]

Problems

1. From the following data calculate the heat balance for a certain boiler plant: Coal fired, 5,000 lb. per hr.; water fed to boiler, 40,000 lb. per hr. at 200°F.; steam, 580°F. at 250 lb. per sq. in. abs.; flue gas, 650°F. The coal had the following analysis: C, 76.3; H_2, 4.8; O_2, 4.0; N_2, 0.7; S, 1.1; ash, 9.7; moisture, 3.4; 12,800 B.t.u. per lb. The cinder analysis was ash, 71.5; combustible, 28.5. The flue gas analysis was CO_2, 13.1; O_2, 5.7; CO, 0.6; N_2, 80.6. Assume 1 hr. and 60°F. as the datum line for the basis of calculations.

2. A roasting oven is fired with coal containing 8 per cent moisture, 21.0 per cent volatile combustible, 62 per cent fixed carbon, and 9.0 per cent ash with a heating value of 13,200 B.t.u. per lb. Refuse taken from the ashpit contains 10.0 per cent moisture, 9.0 per cent volatile combustible, 26.6 per cent fixed carbon, and 54.4 per cent ash. Calculate the percentage of the heating value of the coal that is lost by the presence of unburned combustible matter in the refuse.

3. Explain exactly how each of the following factors affects the efficiency, furnace temperature, and stack temperature of a steam boiler:

a. Insufficient air.
b. Excess air.
c. Leaky furnace settings.
d. Tube deposits.

4. A furnace fired with a hydrocarbon fuel oil has a dry stack gas analysis of 12.1 per cent CO_2, 6.1 per cent O_2, and 81.8 per cent N_2. Calculate,

a. Composition of original fuel oil.
b. Percentage of excess air used.
c. Cubic feet of air (s.t.p.) per pound of fuel.

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[1] For equipment, see Perry, *op. cit.*, pp. 1092–1118.

CHAPTER VI

THE DESTRUCTIVE DISTILLATION OF COAL

When coal is distilled by heating without contact with air, it is converted into a variety of solid, liquid, and gaseous products. The nature and amounts of each product depend upon the temperature used in the decomposition and the variety of coal. In ordinary practice, coke-oven temperatures are maintained above 900°C. but may range anywhere from 400 to 1000°C. The principal product by weight is coke. If a plant uses temperatures from 400 to 750°C., the process is termed *low-temperature* carbonization; with temperatures above this it is designated as *high-temperature* carbonization. In the low-temperature carbonization the quantity of gaseous products is small and that of the liquid products is relatively large, while in high-temperature carbonization the yield of gaseous products is larger than the yield of liquid products, with the production of tar being relatively low. In addition to coke, the solid products recovered are ammonium salts, naphthalene, anthracene, and "cyanogen" compounds; the liquid products are water, tar, and the various oils; the gaseous products are hydrogen, methane, ethylene, carbon monoxide, carbon dioxide, hydrogen sulfide, ammonia, and nitrogen. The products other than coke are collectively known as *by-products.*

The destructive distillation of coal, or its carbonization, is really a striking example of the *unit process of pyrolysis.* Most of this chapter will be concerned with the equipment needed to carry out, on a commercial scale, the basic chemical changes that take place. The chemical theory of the pyrolysis of coal[1] indicates the following in a step-by-step decomposition:

1. As the temperature is raised the aliphatic "carbon to carbon bonds are the first to break."
2. "Carbon to hydrogen linkages are severed next as the temperature of 600°C. is approached and exceeded."
3. "The decompositions during carbonization are essentially reactions effecting the elimination of heterocycle complexes and progressive aromatization."
4. "The average molecular weights of the volatile intermediate products constantly decrease as the temperature of carbonization rises. This

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[1] **Fuchs** and **Sandhoff**, Theory of Coal Pyrolysis, *Ind. Eng. Chem.*, **34**, 567 (1942).

decrease is marked by the evolution of water, carbon monoxide, hydrogen, methane, and other hydrocarbons."

5. "Final decompositions are at a maximum between 600 and 800°C." Fuchs and Sandhoff give several examples of coal pyrolysis of which Fig. 1 is typical.

Historical.—It is known that coke was an article of commerce among the Chinese over 2,000 years ago, and in the Middle Ages it was used in the arts and for domestic purposes. Nevertheless it was not until 1620 that there is any record of producing coke in an oven. In this year Sir William St. John was granted a patent in England for the beehive oven. Up until the middle of the nineteenth century, coal tar and coal-tar products were regarded as wastes, either to be thrown away or burned under coking retorts. About 1845 tar began to be used in Germany for making roofing felt; distillation products of tar were applied through impregnation as a wood preservative. A year or two earlier, in England, coal-tar naphtha had been successfully employed as a solvent for india rubber, a use still common today.

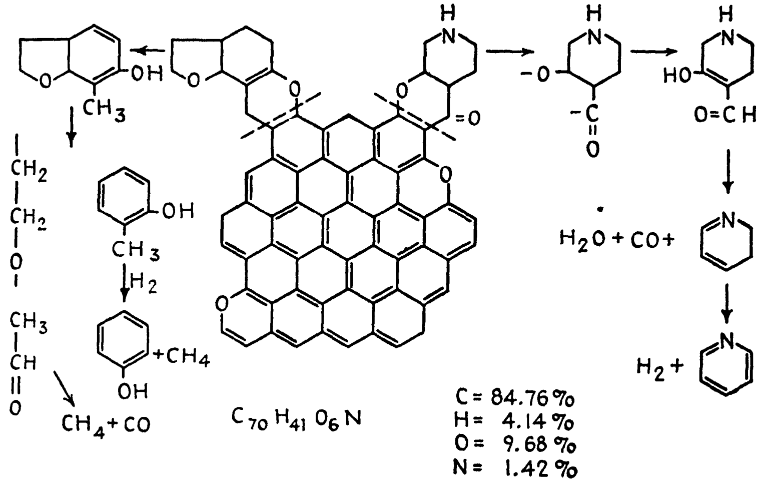

FIG. 1.—Example of coal pyrolysis. (*After Fuchs and Sandhoff.*)

The synthesis of the first coal-tar color, by Sir William Perkin in 1856, caused a great demand for the crude coal tar and it became a commercial product of increasing value. Perkin, by his discovery of the brilliant violet dye mauve (see Chap. XXXVIII), while he was attempting a synthesis of quinine through oxidation of crude aniline in England, laid the foundation of the world's coal-dye industry.

In 1792 the first successful experiment in the production of gas from coal was carried out by William Murdock, the father of the coal-gas industry. The results of this labor made it possible to light the streets of London with gas in 1812. The first rectangle or retort ovens were built in Germany in 1830. In 1835 the first retort coke, with its accompanying gas, was made by William Firnstone at the Mary Ann furnace in Pennsylvania. The first battery of Semet-Solvay ovens was erected in Syracuse, N.Y., in 1893 and was soon followed by ovens of the Otto-Hoffman, Koppers, and Collins types.

TABLE 1.—COMPARISON OF UNITED STATES PRODUCTION OF TAR AND PRODUCTION AND SALES OF CERTAIN CRUDES, AVERAGE 1934–1938, ANNUALLY 1939 AND 1940, U.S. TARIFF COMMISSION

(Production and sales in thousands of gallons; value in thousands of dollars)

Product	Average 1934–1938	1939	1940	Increase, 1940 over 1939, per cent
Tar produced	488,407	554,406	673,287	21.4
Benzol:				
Production	22,376	30,470	36,556	20.0
Sales	20,273	26,628	33,376	25.3
Sales value	$2,822	$3,618	$4,305	19.0
Motor benzol:				
Production	70,306	86,246	101,140	17.3
Sales	69,303	81,672	95,330	16.7
Sales value	$6,363	$7,679	$8,038	4.7
Naphthalene:				
Production[a]	68,935	104,086	159,637	53.4
Sales[a]	61,618	87,837	145,914	66.1
Sales value	$1,239	$1,517	$2,920	92.5
Creosote oil:				
Production	92,397	110,242	119,679	8.6
Sales	93,332	101,487	107,716	6.1
Sales value	$10,140	$12,385	$13,030	5.2
Toluol:				
Production	17,571	24,355	30,440	25.0
Sales	17,269	24,683	29,524	19.6
Sales value	$4,568	$4,952	$7,298	47.4

[a] Thousands of pounds.

Uses and Economics.—As would be expected, the largest yield from the distillation of coal is that of coke, and by far the most important use of coke is in the blast furnaces of the metallurgical industries. The 1943 coke production was 70,568,944 tons with 8,274,035 of this total supplied by the beehive ovens.[1] Not many years ago, actually in 1918,

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[1] "Mineral Industry Surveys," No. 1092, U.S. Bureau Mines, Washington, 1943.

TABLE 2.—PRODUCTION OF CRUDE PRODUCTS FROM COAL TAR IN 1940, U.S. TARIFF COMMISSION

Product	Production (quantity)	Sales		
		Quantity	Value	Unit value
Tar, gal	673,286,517	350,691,110	$16,051,496	$0.046
Light oil and derivatives:				
Crude light oil, gal	216,617,985	10,324,670	829,031	0.080
Benzol (except motor benzol) gal.	36,555,643	33,376,216	4,304,574	0.129
Motor benzol, gal	101,140,079	95,329,911	8,037,526	0.084
Toluol, crude and refined, gal	30,440,324	29,524,248	7,297,790	0.247
Solvent naphtha, crude and refined, gal	9,230.139	8,496,302	1,519,039	0.179
Xylol, gal	5,645,993	5,335,574	1,239,603	0.232
Other light oil products, gal	11,689,253	9,561,159	956,102	0.100
Naphthalene, crude (solidifying under 79°C.), lb	159,637,499	145,914,455	2,920,029	0.020
Anthracene, crude (less than 30 per cent), lb				
Cresylic acid, crude (less than 75 per cent), gal				
Cumene, gal				
Pyridine, crude and refined, gal	241,075	218,165	296,441	1.359
Creosote oil, gal	119,678,785	107,715,986	13,030,307	0.121
Coal tar sold or consumed in coal-tar solution, gal	4,215,152	4,274,152	249,224	0.058
Tars, crude and refined, gal	25,718,000	23,173,506	1,678,895	0.072
Tars, road, gal	150,523,083	152,737,701	10,511,926	0.069
Other distillates, gal	50,631,609	13,091,194	1,983,027	0.151
Pitch of tar, tons	707,082	391,741	4,988,049	12.733
Pitch of tar coke, tons	90,906	87,177	1,009,219	11.580
Total	....	....	77,258,333	

	Gallons	Value	Unit value
Tar distilled by purchasers thereof:			
Oil-gas tar	5,247,209	$235,766	$0.045
Water-gas tar	41,579,643	1,830,923	0.044
Coal tar	299,965,061	15,461,612	0.052
Total	346,791,913	17,528,301	0.050

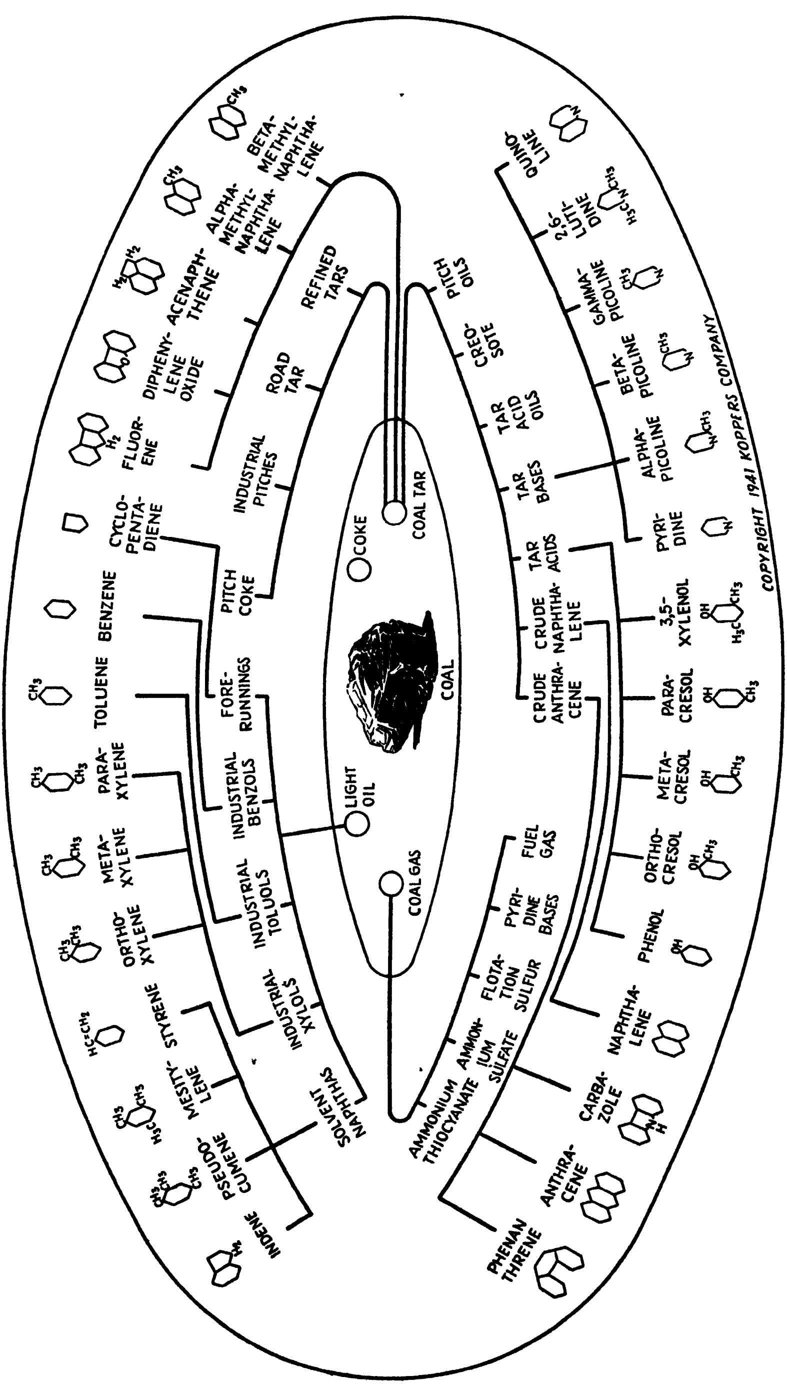

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FIG. 2.—How many grandchildren has a lump of coal? *(Courtesy of the Koppers Co.)*

the beehive ovens produced[1] a greater proportion of coke then came from the by-product ovens.

The liquid products, comprising coal tar and ammonia liquor, although not so large in volume, are at least as important industrially as the solid products of coal distillation. Hence the importance of the by-product ovens. The coal-tar products are made into dyes, intermediates, medicinals, flavors, perfumes, resins, rubber chemicals, and thousands of other useful products that are almost indispensable in our present-day civilization. Table 1 shows the production of coal tar and crudes from 1934 to 1940. The upswing in by-product coke oven operation in 1940 was due in a large measure to the demand created by the Second World War for coke for metallurgical purposes. The distribution of the domestic production and sales of coal tar, crude light oil, and crude products made from them, as well as the quantities of the several kinds of tar distilled, is shown in Table 2. The production and sales of intermediate and finished coal-tar products in 1940 are summarized in Tables 2 and 4, Chap. XXXVIII.

An over-all presentation of the multiplicity of valuable products obtained from coal is exhibited by Figs. 2 and 7 and in Table 3. Numerous chapters in this book consider the use and manufacture of many of these products or their derivatives. Coal is not only the country's fundamental fuel but the basic raw material for many essential industries from dyes, medicines, and explosives down to modern plastics.[2]

COKING OF COAL

The two main types of coking procedures are the beehive and the by-product. Beehive coking is the old and primitive method of securing coke for metallurgical purposes. In it the by-products are wasted. The process is also slow. In the by-product ovens the coal charge is heated on both sides so that the heat travels toward the center and thus produces shorter and more solid pieces of coke than is made in the beehive oven. No burning takes place within the oven, the heat being supplied completely from the flues on the sides. About 40 per cent of the oven gas after being stripped of its by-products is returned and burned to supply the heat for coking. However, when a by-product plant is located near a city, all the coke-oven gas is sold for domestic usage. In this case the cheaper producer gas is specially manufactured for heating the by-product ovens.

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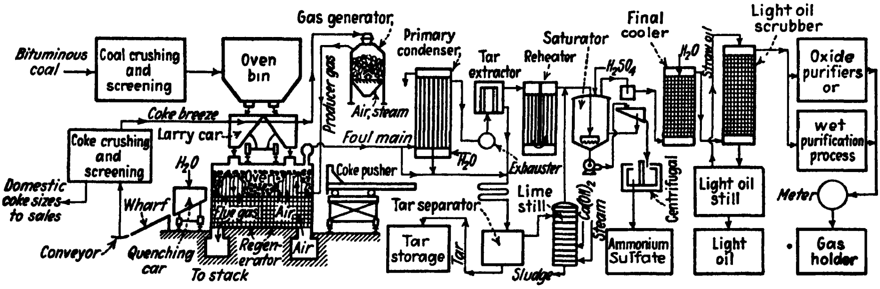
[1] PERRY, *op. cit.*, p. 2326.

[2] WAKEMAN and WEIL, Coal as a Source Material for the Plastics Industry, *Ind. Eng. Chem.*, **34**, 1387 (1942); GUY, Agricultural Uses of Coal and Its Products, *Ind. Eng. Chem.*, **35**, 139 (1943); HOWARD, Possible New Uses for Coal, *Ind. Eng. Chem.*, **35**, 156 (1943); STAFF, Coal Research Laboratory of Carnegie Institute of Technology, Coal an Abundant Raw Material for New Chemicals, *Chem. Industries*, **52**, 202 (1943).

Formerly much coal was distilled in small retorts primarily for the production of domestic coal gas. The coke formed was used to furnish heat for the retorts. However, this practice has been largely discontinued in favor of coke-oven gas.

Beehive Coking.—This oven consists of a beehive-shaped brick chamber, with either a flat or inclined floor, provided with a charging hole at the top of the dome and a discharging hole in the circumference of the lower part of the wall. The coal is introduced through the hole in the dome and spread over the floor in the oven to a height of about 2 ft. The heat retained in the oven is sufficient to start the distillation. The gases given off from the coal mix with the air entering at the top of the discharge door and burn; the heat of combustion is sufficient for the pyrolysis and distillation. The products of combustion pass out the top of the oven. Since the charge is heated mainly from top side, carbonization proceeds relatively slowly and the coking time varies from 48 to 72 hr. The coking rate at the start is about 1 in. per hr. Because of this slow heat penetration, the coal employed must be of the strongly coking variety to ensure that the binding ingredients in the lower part of the charge are not decomposed before being called upon to function as a binder. During the coking process strongly coking coals may expand as much as 8 in.



Bituminous coal	1 ton	To produce	10-12.5 M cu ft 550 B.t.u. gas
Sulfuric acid (60° Bé)	25 lb.		1,400 lb. coke
Lime	1½-2 lb.		10 gal. tar
Water	1,000-2000 gal		25 lb. ammonium sulfate
Steam	400-600 lb.		2.0-4.0 gal. light oil
Electricity	6-9 kw-hr		
Direct labor	0.7-1.5 man-hr.		

FIG. 3.—By-product coke-oven procedures.

In spite of the loss of volatiles in the ordinary beehive procedures, many such ovens are in use at the present time, owing chiefly to a decided preference for the hard, strong, and cellular beehive coke on the part of certain metallurgical coke users. The capital required is also relatively low. But the greater return from valuable products places the beehive at a disadvantage except perhaps to help in supplying peak demands, such as prevail during war.

By-product Coking.—The by-product coke oven is a narrow chamber usually about 38 to 40 ft. long, 10 ft. high, and tapering in width from 17 or 18 in. at one end to 15 or 16 in. at the other. The average oven holds about 12 tons of coal, although some of the larger ovens hold as much as 16 tons. These ovens are used for carbonizing coal only in large amounts and are built in batteries of 30 to 90 ovens. The general arrangements for the operation of a by-product coke oven with its various accessories, followed by the initial treatment of its by-products, are depicted[1] in Fig. 3.

The by-product coke oven is one of the most elaborate and costly of masonry structures and is erected with the closest attention to engineering details so that it can withstand the severe strains incurred in its use. The oven block is built of refractory brick with heating flues between the coking ovens as shown in Fig. 4. There are various accessories for support, foundation, and heat insulation with regenerative chambers underneath for waste-heat utilization.

The *individual* by-product coke oven is intermittent in its operation but each oven is started and finished at different times so that the operation of the entire block produces continuously a gas of good average composition. A charge of finely crushed coal is dropped from a lorry car through charging holes (usually four, though the generalized flow sheet of Fig. 3 shows only two) in the top and into the oven where the walls are approximately at 2000°F. The first rush of gas, steam, and air is allowed to escape to the air through an outlet valve in the uptake pipe which rises from the top of the oven. The surface of the coal is leveled in the oven and the charging holes are then covered. Heating is carried on and the charge left in the oven until it is completely coked and the evolution of the volatile matter has ceased. The average temperature at the center of the charge at the end of the heating period is usually about 1800°F., while the average flue temperature is about 2350°F. The temperatures vary with the conditions of operation, the coking time, the width of the oven, the kind of coal, its moisture content, and fineness of division.

At the end of the coking time the doors on the ends of the oven are opened and the entire red-hot mass is pushed out in less than a minute by a ram electrically driven through the oven from end to end. The coke falls into a quenching car which holds the charge from one oven. This car travels to a quenching station where an overhead nozzle sprays about 6,000 gal. of water into it. The car after draining for a minute is then moved to a coke wharf where the coke is dumped from the bottom of the car onto conveyors which take it to a crushing and screening plant.

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[1] See also Pictured Flow Sheet, Byproduct Coke Plant, *Chem. & Met. Eng.*, **48**, No. 12, 104 (1941).

Very often, instead of water, an inert gas (as CO_2 or N_2) is used to cool the coke, called *dry quenching*. Seventy to seventy-five per cent of the heat in the coke may be thus recovered, and it is claimed that the coke obtained gives better fuel efficiency than wet-quenched coke.[1]

The gas from the destructive distillation of the coal, together with entrained liquid particles, passes upward through a cast-iron gooseneck into a horizontal steel trough which is connected to all the ovens in a series. This trough is known as the *hydraulic main* or collecting main. A slight suction is maintained on the main by means of a mechanical exhauster beyond the primary condenser. The tar, overlaid by an aqueous liquid containing ammonia and its compounds, collects in the bottom of the main. The liquids in the main are pumped away as they collect, though part of the liquid may be recirculated for cooling flushing.

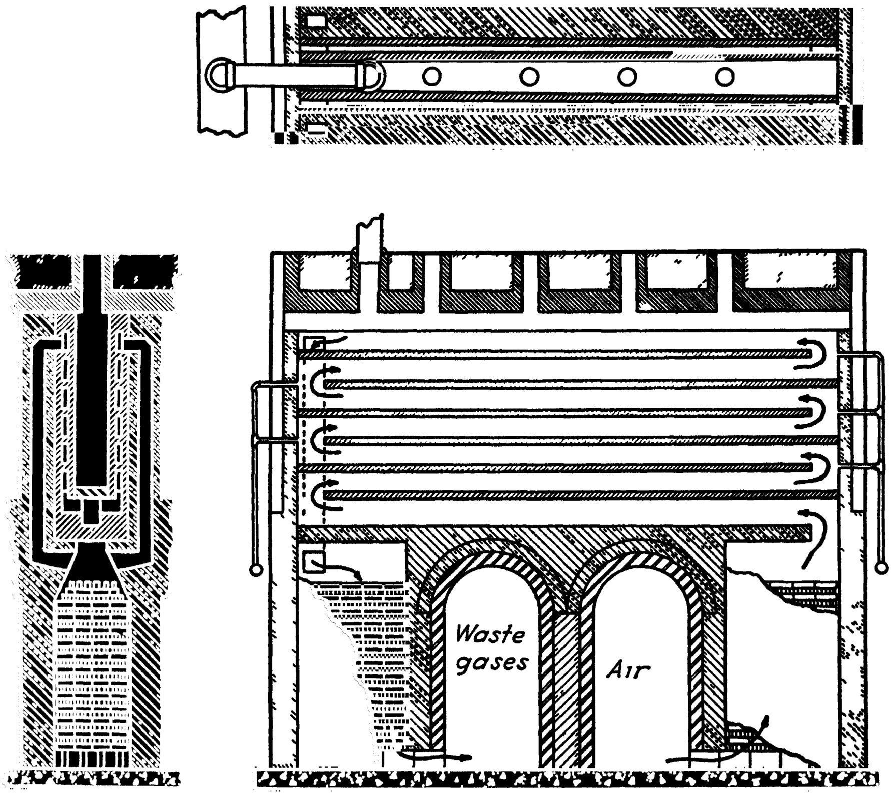

FIG. 4.—Semet-Solvay by-product coke oven.

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[1] *Intern. Conf. Bituminous Coal*, 2d conf., **2**, 692 (1928), Carnegie Institute of Technology, Pittsburgh.

TABLE 3.—APPROXIMATE YIELDS[a] PER TON OF COAL CARBONIZED
(Depending on coal and conditions used)

	High temperature	Low temperature
Furnace coke	1,300–1,550 lb.	
Coke breeze	70–100 lb.	
Semicoke (12 per cent volatiles)	....	1,500 lb.
Tar	8–12 gal.	30 gal.
Ammonium sulfate	17–25 lb.	10 lb.
Light oil (removed from gas by oil scrubbing)	2–4 gal.	2 gal.
Gas (550 B.t.u.)	10,000–12,500 cu. ft.	
Gas (950 B.t.u.)	....	3,000 cu. ft.

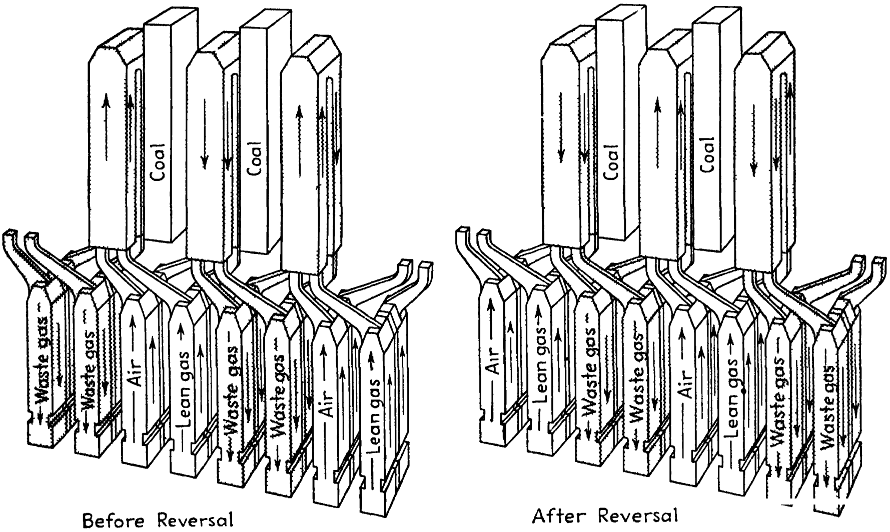
[a] PERRY, *op. cit.*, pp. 2338–2339. See FIG. 3, also. Note that 4 lb. of technical ammonium sulfate are equivalent to 1 lb. of ammonia.

The *types of oven* differ mainly in the arrangement of their heating flues, whether vertical or horizontal, the method of applying the regenerative principle to preheating the air for combustion, and also in the arrangement for introducing the heating gas and air to the flues. In yields, qualities of products, and methods of operation there is no material variation in the several by-product coke ovens. The important differences among the types of ovens will be taken up briefly.

The Semet-Solvay oven is the only horizontal-flued oven that has survived to the present time (see Fig. 4). It was a pioneer in the by-product coking industry and did much toward developing the art and overcoming the strong prejudices among the coke users in the early days of the industry. These ovens have two distinctive features: (1) They are heated by flames burning horizontally and serially instead of vertically and in parallel as in most ovens. (2) Though built in batteries, each oven is structurally independent of the others. Each oven has its heating flues separated from those of the adjoining oven by a solid wall of firebrick. Each oven has its individual regenerator if regenerative heating is used. In regeneration, reversal is made from end to end only between the air and waste gases while the fuel gas burns continuously at all burners.

The Koppers-Becker ovens are the most widely used, vertical-flued ovens in America. The flow of gases is shown in Fig. 5. These ovens are all of the regenerative type and have individual regenerators from end to end, parallel with the longitudinal axis but underneath the oven. The reversal of the air and waste gas flow is made from end to end every half hour. Two characteristics of the Koppers ovens are individual control of the heating conditions in each flue through separate means of adjustment of the fuel gas, air supply, and draft, with the individual regenerators introducing heated air directly at the base of each individual heating flue. Recently there has been introduced a newer type of the Koppers regenerative oven in which the reversal of flow is not end to end but side to side; *i.e.*, from the flues on one side of an oven to those on the other through cross ducts in the brickwork above and below the oven. This eliminates the irregularities of temperature caused by the usual end-to-end system of reversal. The gas burns upward, crosses over the top of the oven, comes downward on the other side, and exits through the regenerative oven underneath. This travel is completely reversed periodically.

Other ovens that are used in the United States are the Otto-Hoffmann, Otto-Schniewind, the Foundation, the Piette, the Roberts, the Piron, and the Kloenne. These ovens have not had the general acceptance that the Koppers and Semet-Solvay ovens have had. They are all of the vertical-flued regenerative type with the exception of the Roberts which is a "flueless" type in which the gas and air are introduced vertically downward.



Before Reversal

After Reversal

Fig. 5.—Koppers-Becker by-product oven. The flow of air and gas in the flues and regenerators in the compound oven when fired by lean gas, before and after reversal.

Recovery of By-products.—The gaseous mixture leaving the oven is made up of permanent gases which form the final purified coke-oven coal gas for the market, accompanied by condensible water vapor, tar, and light oils, with solid particles of coal dust, heavy hydrocarbons, and complex carbon compounds. The gas is passed from the foul main (Fig. 3) into the primary condenser and cooler at a temperature of about 75°C. Here the gases are cooled by means of water to 30°C. The gas is conducted to an exhauster which serves not only to compress the gas but also to remove about 75 per cent of the tar in it because of the high-speed swirling motion imparted to the gas. During the compression the temperature of the gas rises to as high as 50°C. The gas is passed to a final tar extractor where the tar is thrown out by impingement of gas jets against metal surfaces. On leaving the tar extractor the gas carries three-fourths of the ammonia and 95 per cent of the light oil originally present when leaving the oven.

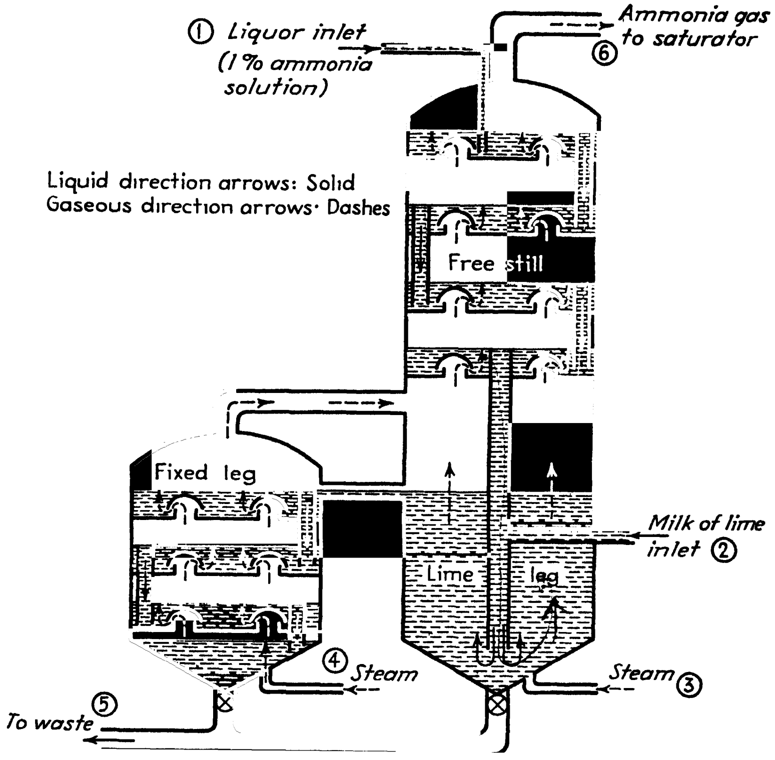


Fig 6 —Diagram of an ammonia still. This operates with drain from fixed leg open sufficiently to prevent accumulation of liquor in this section. Drain from lime leg is closed except for cleanout.

The gas is led to a *saturator* (see Fig. 3) which contains a solution of 5 to 10 per cent[1] sulfuric acid, where the ammonia is absorbed with the formation of solid and crystalline ammonium sulfate. The saturator is a lead-lined closed vessel where the gas is fed in by a serrated distributor underneath the surface of the acid liquid. The acid concentration is maintained by the addition of 60°Bé. sulfuric acid and the temperature is kept at 60°C. by the reheater and the heat of neutralization. The crystallized ammonium sulfate is removed from the bottom of the saturator by a compressed air injector, or centrifugal pump, and is drained on a table from which the mother liquor is run back into the saturator. The salt is dried in a centrifuge and bagged, usually in 100-lb. sacks (see Chap. XX).

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[1] At the start of a charge, the acidity is often as high as 25 per cent, but ammonium bisulfate is liable to be formed when free sulfuric acid exceeds 10 to 11 per cent.

If it is not desired to get ammonium sulfate, aqua ammonia may be made by scrubbing the gas coming from the tar extractor with cold water in a bubble-cap tower or in a spray chamber through which the gas is passed countercurrent to the liquid, or by means of a rotary scrubber in which the gas is forced through a space in which large fresh surfaces of washing liquor are being constantly turned up by a vane or brushes on a rotating shaft. The solution obtained in this way contains about 1 per cent of ammonia and must be distilled and strengthened before it can be shipped or marketed. The ammonia still used is somewhat like that employed for the recovery of the ammonia in the Solvay process for making soda ash (see Chap. XV). Details of such an ammonia lime still are given in Fig. 6. Here the "limeleg" must be used to liberate that large part of ammonia which is fixed in the form of chloride[1] and other salts. In the usual case, as depicted in Fig. 3, some weak ammonia liquor is separated from the tar. This is distilled with lime and steam as shown in Figs. 3 and 6, the ammonia gas in this case going into the saturator.

The gas leaving the saturator at about 60°C. is taken to final coolers or condensers where it is scrubbed with water until its temperature is 25°C. During this cooling some naphthalene separates and is carried along with the waste water and recovered. The gas is passed into a *light oil or benzol scrubber* (Fig. 3) over which is circulated, at about 25°C. as the absorbent medium, a heavy fraction of petroleum called *straw oil*, or sometimes a coal-tar oil. The straw oil is sprayed in the top of the absorption tower while the gas flows up through the tower. Although wooden grids are generally used as a filling material, spiral rings have been employed recently. The straw oil is allowed to absorb about 2 to 3 per cent of its weight of light oil with a removal efficiency of about 95 per cent of the light oil vapor in the gas.

The rich straw oil, after being warmed in heat exchangers by vapors from the light oil still and then by hot debenzolized oil flowing out of the still, is passed to the stripping column, where the straw oil, flowing downward, is brought into direct contact with live steam. The vapors of light oil and steam pass off and upward from the still through the heat exchanger previously mentioned and to a condenser and water separator.

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[1] *Cf.* PERRY, *op. cit.*, p. 1370.

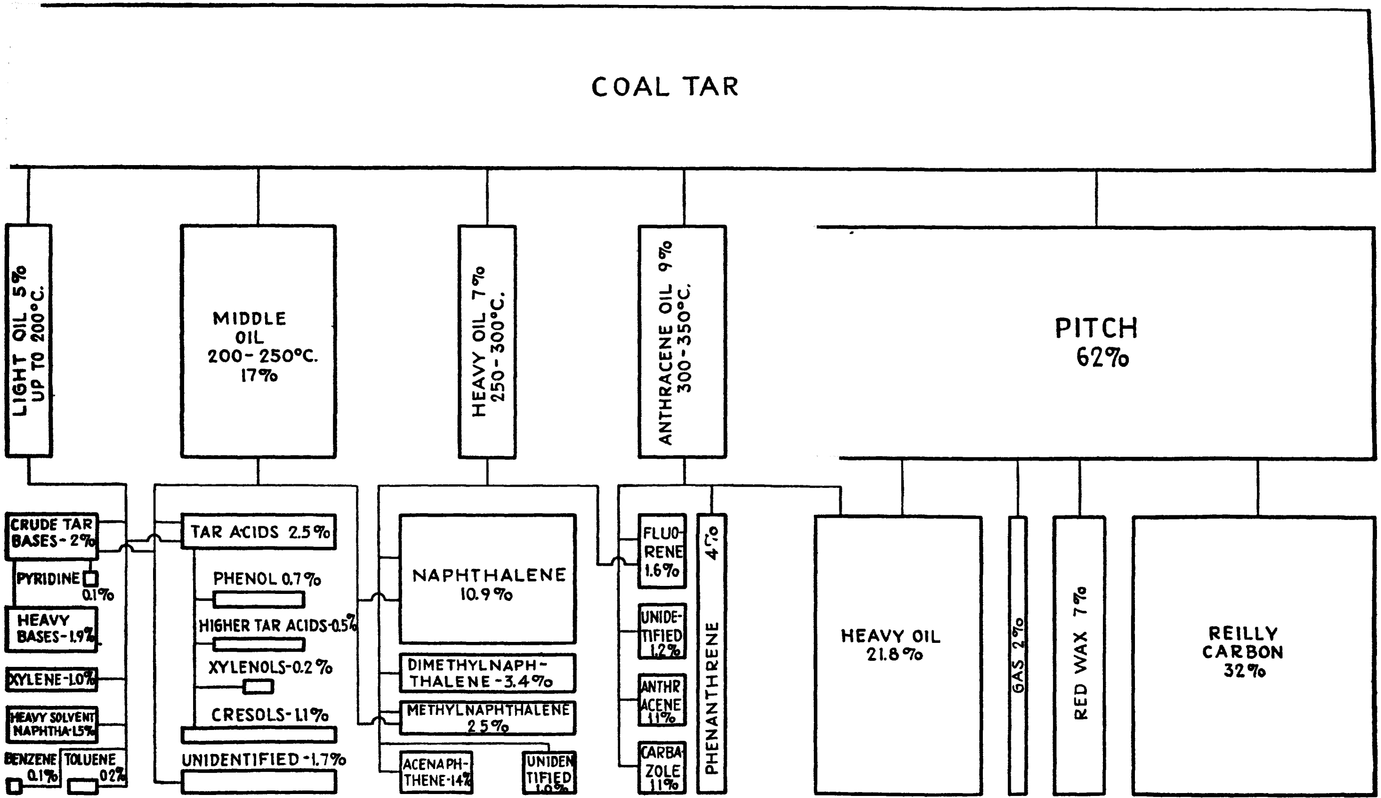

FIG. 7.—Principal products from coal tar. The crude coal-tar distillates as obtained in practice and the products derived therefrom. The percentage yields as shown and represented by the areas of the rectangles are average values based on the original tar. (*Courtesy of Reilly Tar & Chemical Corporation.*)

The lean or stripped straw oil is returned through the heat exchanger to the scrubbers.

The crude *light oil* is distilled in the crude fractionating tank stills of 6,000 to 15,000 gal. capacity provided with short towers (see Fig. 8). These are batch stills and are heated first with indirect steam coils and later by direct steam to drive over the heavier fractions. If pure benzene, toluene, and solvent naphtha are desired, several fractions from the crude fractionating still are made and each of these fractions is redistilled in the fractionating still of Fig. 8. For motor fuel only one cut is made from the crude still. The crude products are washed with strong sulfuric acid to remove unsaturated impurities, next with caustic soda and water. The washed products are finally redistilled to remove any complex polymers formed by the action of any acid that might remain dissolved in the benzene. Note from Fig. 3, that coal furnishes both light oil and coal tar and, from Figs. 7 and 8, that the distillation of coal tar furnishes further amounts of light oil. These two fractions are usually united and rectified.

TABLE 4.—TYPICAL COMPOSITION OF LIGHT OIL FROM GAS[a]

	Gallons per Ton of Coal
Benzene	1.85
Toluene	0.45
Xylene and light solvent naphtha	0.30
Acid washing loss (mostly unsaturateds)	0.16
Heavy hydrocarbons and naphthalene	0.24
Wash oil	0.20
Total crude light oil	3.20
Pure motor fraction	2.50

[a] PORTER, "Coal Carbonization," Reinhold Publishing Corporation, New York, 1924. See PERRY, *op. cit.*, pp. 2371 and 2372 for tabular presentation of more details.

The gas after being stripped of its ammonia and light oil has the sulfur removed in purifying boxes which contain iron oxide on wood shavings or in wet scrubbing towers as is the best present-day practice. These procedures are fully described in Chap. VII on Fuel Gases.

Low-temperature Carbonization.[1]—During the present century there has been a large amount of experimental work carried out on the carbonization of coal at temperatures ranging from 400 to 600°C., with the main object to obtain maximum yields of liquid products and to produce semicokes containing from 8 to 20 per cent volatile matter. Here again the characteristics and yields of the various products depend upon the coal, the temperature, and the treatment. Tables 3 and 5 show the difference in gas content and in yield products for high- and low-temperature

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[1] BROWNLIE, Low-temperature Carbonization, *Ind. Eng. Chem.*, **19**, 39 (1927), and eight preceding articles.

TABLE 5.—VARIATION OF GAS FROM LOW- AND HIGH-TEMPERATURE COAL CARBONIZATION[a]

Gases	Coking temperature, 500°C., per cent	Coking temperature, 1000°C., per cent
CO_2	9.0	2.5
C_nH_m	8.0	3.5
CO	5.5	8.0
H_2	10.0	50.0
CH_4 and homologs	65.0	34.0
N_2	2.5	2.0

[a] ROBERTS and JENKNER, "International Coal Carbonization," p. 198, Sir Isaac Pitman & Sons, Ltd., London, 1934.

systems. At the present time the low-temperature carbonization coal has only recently emerged from the experimental stage and is of no great industrial importance in the United States although it has been commercial in England for some time.

Unit Operations and Unit Processes.—As Chap. II points out, chemical engineering can be "resolved into a coordinated series of unit physical operations and unit chemical processes." The various flow sheets as presented in this book will frequently be broken down into such a sequence of unit operations (Op.) and unit processes (Pr.). These cause continuous attention to be directed to the unitary aspects of the various operations or processes, with the consequent transfer of the experience gained with given unit operation in one field to the same operation in another. Several of the flow sheets presented in this chapter are rather complicated, more so than in similar presentations in other sections of the book. However, Fig. 3 can be divided into different steps representing the flow of material through the various pieces of equipment wherein the proper unit operation or unit process takes place. The listing of these unitary aspects is in a sense the synopsis of the particular process. Figure 3 may be thus broken down into the following unit operations (Op.) and unit processes (Pr.):

Coal is transferred, crushed, and screened (Op.).
Coal is charged to a hot empty oven (Op.).
Coal is chemically transformed to coke and volatiles by pyrolysis (Pr.).
Hot coke is pushed out of oven, quenched, and transported (Op.).
Condensable products of distillation are liquefied and collected in hydraulic main (Op.).
Foul gas is cooled and tar extracted (Op.).
Ammonia is removed from gas as ammonium sulfate (Pr.).
Gas is cooled and subjected to benzol and toluol removal by absorption in straw oil (Op.).

Hydrogen sulfide is removed (Pr.).
Purified gas is metered and transferred to consumers (Op.).

The tar separated from the hydraulic main and the tar extractor is settled from ammonia liquor and subjected to the sequences represented by flow sheet, Fig. 8.

DISTILLATION OF COAL TAR

Coal tar is a mixture of many chemical compounds, mostly aromatic, which vary widely in composition (see Figs. 2 and 7).[1] It is essentially a by-product of the destructive distillation or pyrolysis of coal. Depending upon whether the primary objective is coal gas or coke and also on the nature of the coal, the amount of crude tar (with a specific gravity from 1.0 to 1.2) obtained varies from 8 to 12 gal. of tar per ton of coal. A typical tar composition is listed on the bottom of Fig. 8, where the steps to separate coal tar into these constituents are depicted. The objects of distillation are to produce the maximum yields of the valuable products with a minimum of free carbon in the pitch. These products must usually be sharply fractionated with a minimum of overlapping. The process also should be thermally economical.

Methods of Distillation.—There have been many improvements in coal-tar distillation in the past few years; in general it may be stated that the trend is away from the simple batch still and toward modifications that will give the highest yields of the various "oils." There are at present in use a number of major types of stills such as batch stills, vacuum stills, steam-operated stills, gas recirculated stills, coke stills, and pipe stills.

Table 6.—A Comparison of Coal-tar Stills[a]

System	Temperature, degrees C.	Pitch, per cent	Oil, per cent	Free carbon, per cent
Atmospheric still	413	57.8	40.1	40.7
Vacuum still	330	42.5	56.6	23.8
Steam distillation	340	47.5	50.6	28.8
Recirculating inert gas (CO_2) through still	358	46.9	52.6	29.0
Recirculating inert gas (N_2) through still)	331	46.4	52.0	27.2

[a] Weiss, The Distillation of Coal Tar, *J. Soc. Chem. Ind.*, **51**, 219 (1932).

1. *Batch Stills.*—As might be imagined from their simplicity of operation, fire-heated batch stills were the first type of equipment used in tar distillation. Varying in size from 3,000 to 7,000 gal., they consist essen-

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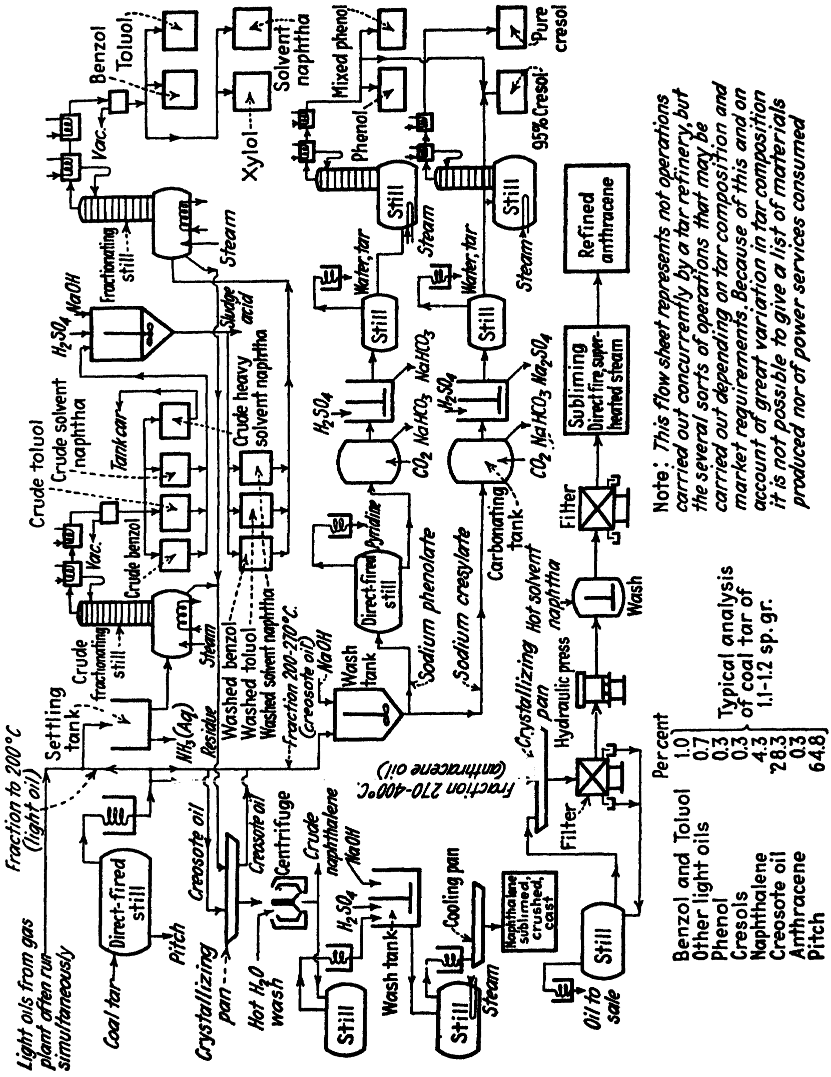
[1] Also Perry, *op. cit.*, pp. 2374–2376.

tially of a large iron container with connection to a condenser, into which the tar is dumped and heat applied until the distillation is complete, as shown in Fig. 8. In the United States, a horizontal type of still is preferred, although on the continent vertical stills are in general use.



Note: This flow sheet represents not operations carried out concurrently by a tar refinery, but the several sorts of operations that may be carried out depending on tar composition and market requirements. Because of this and on account of great variation in tar composition it is not possible to give a list of materials produced nor of power services consumed

	Percent	
Benzol and Toluol	1.0	Typical analysis of coal tar of 1.1-1.2 sp. gr.
Other light oils	0.7	
Phenol	0.3	
Cresols	0.3	
Naphthalene	4.3	
Creosote oil	28.3	
Anthracene	0.3	
Pitch	64.8	

FIG. 8.—Summarized diagrammatic flow sheet of coal-tar products.

The essential disadvantages of the batch still is discontinuous operation, with the pitch residue remaining in the still and being subject to heat during the entire period of distillation. This disadvantage may be somewhat overcome by some form of air or steam agitation to increase tar velocity and improve heat transfer. Steam is preferred. In the ordinary batch still, the procedure is of relatively long duration and the fractionation is not very sharp. When the temperature rises to between 500 and 700°F., during the anthracene condensation, the residue in the still remains for a long time in contact with highly heated surfaces, causing local overheating and decreased oil production, and furnishing a pitch containing considerable portions of free carbon.

2. *Vacuum Stills.*—The object of vacuum distillation is to lower the final tar temperatures and thereby increase the yield of oils. Of necessity, special precautions, which include heavier retort shells and internal reinforcement, should be observed. Vacuum distillation has been adopted with the idea of protecting the tar by reduction of the distillation temperature. Under vacuum distillation some difficulty is met in condensing the low-boiling oil fractions.

3. *Steam-operated Stills.*—The use of sufficient steam to agitate the tar does not involve an amount of steam sufficient to affect the thermal distillation in any way; the use of larger volumes of steam, however, will materially lower the still temperature and give higher oil yields. In practice the operation means higher cost for steam and cooling water. In steam distillation, the great danger is that the pitch temperature might drop to such an extent that the use of direct steam would prove very costly.

4. *Gas Recirculated Stills.*—Since air exerts a deleterious oxidizing effect if used for stirring tar mixtures, Weiss in 1922 proposed the use of inert gas recirculated in a closed system.

5. *Coke Stills.*—The general principle here employed involves contacting the tar with raw, hot coke-oven gas, thereby utilizing the sensible heat of these gases to volatilize the tar oils. High yields are obtained at little or no fuel expense.

6. *Pipe Stills.*—The most recent developments in coal tar distillation have been made in pipe still operation. The pipe still has been used for some time in America for the distillation of petroleum, and it is now being successfully adapted for the distillation of tar.[1] It consists essentially of a battery of tubes, arranged within a furnace, through which the tar to be distilled is passed at a relatively high rate in a continuous stream. Thus its construction is similar to that of a water tube boiler, minus the steam drums. Since the tar remains in the heating coils only sufficiently long (a few minutes) for it to be raised to the requisite temperature for distillation, there is no overheating and the minimum proportion of free carbon is produced. Further, the presence of the lower boiling tar constituents in the continuous heating process causes a *lowering* of the boiling points of the high-boiling fractions, so that the time element is

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[1] GROUNDS, Tar Distillation, *Gas World*, **107**, No. 2813, 77–80 (1938).

not only reduced, but the heating temperature also, making the use of the vacuum unnecessary.

Modern practice, as exemplified by the pipe still, is producing such clean-cut fractions that often little further purification is necessary. However, below are given the fractions obtained in an ordinary batch still, and a brief outline of purification as illustrated in Fig. 8 (see also Fig. 7). The yields from different coal tars vary. This explains the differences between the quantities listed in Figs. 7 and 8.

a. *Light oils*[1] usually embrace the cut up to 200°C. They are first crudely fractionated and agitated at a low temperature with concentrated sulfuric acid, neutralized with caustic soda, and redistilled, furnishing benzene, toluene, and homologs.

b. *Middle oils*, or *creosote oils*, generally are the fraction from 200 to 250 or 270°C., which contains naphthalene, phenol, and cresols. The naphthalene settles out upon cooling, is separated by centrifuging, and is purified by sublimation. After the naphthalene is removed, phenol and other tar acids[2] are obtained by extraction with a 10 per cent caustic soda solution and neutralization or "springing" by carbon dioxide. These are fractionally distilled, as shown in Fig. 8.

c. *Heavy oil* may represent the fraction from 250 to 300°C., or it may be split between the middle oil and the anthracene oil.

d. *Anthracene oil* usually is the fraction from 270 or 300°C. up to 350 or 400°C. It is washed with various solvents to remove phenanthrene and carbazole; the remaining solid is anthracene.

MISCELLANEOUS USES OF COAL TAR

Much coal tar is burned for fuel after heating[3] to reduce its viscosity and facilitate its spraying into the furnace. In countries other than the United States where motor fuels are not so abundant, coal tars are hydrogenated[4] producing lighter boiling hydrocarbons.

Coal tars have been studied regarding their pyrolysis[5] products and offer a future source for motor fuel. In the United States much coal tar is consumed on roads and roofs.[6] For this purpose the tar is distilled up to the point where thermal decomposition starts. This "base tar" is oiled back with creosote oil of the proper specification to ensure satisfactory rapid drying but to avoid brittleness in service. Somewhat similar tars are employed to impregnate felt and paper for waterproofing.

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[1] PERRY, *op. cit.*, p. 2371, gives a tabulation of analyses of various light oils.

[2] "Tar acids," in the language of the tar distiller, represent phenol and its homologs which are soluble in caustic soda.

[3] PERRY, *op. cit.*, p. 2357. Fuel value = 15,000 to 16,500 B.t.u. per lb.

[4] HALL and CAWLEY, The Composition of the Products Obtained by the Hydrogenation-cracking of Low-temperature Tar, *J. Soc. Chem. Ind.*, **56**, 303–308T (1937). For a coal-tar hydrogenation flow sheet, see chapter on Hydrogenation, p. 481, by Fenske in GROGGINS, "Unit Processes in Organic Synthesis," McGraw-Hill Book Company, Inc., New York, 1938.

[5] MORRELL, *et. al.*, Cracking Tars and Distillation from Coal, *Ind. Eng. Chem.*, **32**, 39–47 (1940).

[6] HADFIELD, Modern Road Tars, *Gas World*, **108**, 71–75 (1938); KIRBY, Preparation of Road Tars, *Chemistry & Industry*, **1938**, 486–494.

Instead of pyrolyzing or carbonizing coal as described in this chapter, coal is hydrogenated[1] to produce motor fuel in the petroleum-poor countries like England and Germany. This may eventually be one of the processes for motor fuel in the United States when petroleum gasoline becomes scarcer.

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[1] PIER, Coal Hydrogenation, *Ind. Eng. Chem.*, **29**, 140–145 (1937); STORCH, Chemistry of Coal Hydrogenation, *Ind. Eng. Chem.*, **29**, 1367–1371 (1937); GROGGINS, *op. cit.*, pp. 483–484 with flow sheet.

CHAPTER VII

FUEL GASES

The black smoke appearing from countless chimneys in many communities represents a loss of energy in our natural resources and a contamination of the air to the detriment of both animals and plants. The ideal situation would be one in which no coal was burned as such, but where each of its ingredients would be separated and utilized for the purpose *best* suited from a technical viewpoint. In such a case, coke and gas would be the universal fuels, because of their convenience, cleanliness, and efficiency. However, in most cases at the present time, this would make the fuel cost more than for coal. This chapter will consider the various types of fuel gases.

Historical.—The first recorded use of combustible gas was by the Chinese about A.D. 900 when natural gas was piped through bamboo tubes and used for lighting. The first production of coal gas was about 1665 in England and its first utilization was for lighting purposes in 1792. Similar endeavors in this country began in Philadelphia around 1796. It was not long after this that gas companies began to be organized and the manufacture of gas put on a businesslike basis. The dis-

TABLE 1.—PER CENT COMPOSITION AND HEATING VALUES OF VARIOUS FUEL GASES[a]

	Natural gas. (Mid-continent)	Natural gas, (Pennsylvania)	Coal gas (coke oven)	Water gas	Carbureted water gas	Producer gas
Carbon monoxide	.....	....	6.3	43.5	34.0	30.0
Carbon dioxide	0.8	....	1.8	3.5	3.0	3.5
Hydrogen	.....	....	53.0	47.3	40.5	10.0
Nitrogen	3.2	1.1	3.4	4.4	2.9	54.5
Oxygen	.....	....	0.2	0.6	0.5	0.5
Methane	96.0	67.6	31.6	0.7	10.2	1.5
Ethane	.....	31.3				
Illuminants	.....	....	3.7	.....	8.9	
Gross B.t.u. per cu. ft.	967	1,232	586	302	550	135

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[a] MORGAN, "American Gas Practice," p. 30, J. J. Morgan, Maplewood, N.J., 1931. Extensive tables are given on pp. 2363*ff.* of Perty, *op. cit.*, where more properties are tabulated, such as air required and products of combustion.

covery of water gas or *blue gas,* as it is also called, in 1780 and that of producer gas were essential steps in the development of this industry. The exploitation of our natural gas fields gave the final impetus to the gas industry as we know it today.

TABLE 2.—HEATS OF COMBUSTION

Substance	B.t.u. per cu. ft. at 60°F. and 1 atm.		B.t.u. per lb.	
	Gross	Net	Gross	Net
Hydrogen	325	275	61,100	51,623
Carbon monoxide	321.8	321.8	4,347	4,347
Methane	1,013.2	913.1	23,879	21,520
Ethane	1,792	1,641	22,320	20,432
Carbon	....	....	14,093	14,093

NOTE: The net heating value is the practical value since it designates the heat of combusion with the water vapor uncondensed. If the products are cooled to the initial temperature and the water is condensed, its latent heat of condensation is liberated and the larger or gross heating value is obtained. The difference amounts to 18,919 B.t.u. per lb.-mole of water in the products of combustion. *Cf.* PERRY, *op. cit.,* pp. 2378, 2386.

The fuel gas industry is at present undergoing a radical and basic transformation. Coal gas, natural gas, water gas, and even producer gas are not only sources of heat and power, they are already very important raw materials for chemical synthesis. Examples of this will be considered under the specific gas in this chapter, as well as elsewhere in this book, but this statement may here be illustrated by citing the use of water gas as the first step in the manufacture of cheap hydrogen for both inorganic and organic hydrogenations; and of the use of methane or natural gas as a source of hydrogen also, as well as the initial material for synthesis to methanol or for cracking to various types of carbon.

Table 1 summarizes the composition and heating values of the principal fuel gases. The choice in any case is between the composition, heating value, and the cost of producing and distributing the gas. If the gas has to be distributed over more than a short distance, the cheaply made producer gas has too low a B.t.u. content to be competitive with other manufactured gas. The B.t.u. of a gas is a summation of the heats of combustion of its constituents and can be very closely calculated from these. Table 2 summarizes the individual heats of combustion and explains the variation in the heats of combustion of the gases given in Table 1. Flame temperatures obtainable are very important in the utilization of fuel gases. In Perry,[1] the procedure for calculating these is exemplified.

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[1] *Op. cit.,* p. 743.

NATURAL GAS

The seepage from the earth of gases that could be used for lighting was reported in the Ohio Valley as far back as 1775; but the earliest commercial utilization was in Fredonia, N.Y., in 1821. Although natural gas wells may be found widely scattered over the country, the chief fields may be defined as follows: the large Appalachian field covering eastern Kentucky, West Virginia, southern Ohio, eastern Pennsylvania, and part of New York; the Lima field in western Ohio and Indiana; the field that covers southern Oklahoma and northern Texas; the field in the Texas Panhandle; the various Louisiana fields; and finally, those in California. The explanation of the geological occurrence of natural gas and the description of well drilling and development are all beyond the scope of this text.

There are various by-products from raw natural gas that are of industrial significance, such as propane, butane, and natural gasoline. These are separated from the crude gas as liquids by fractionation or absorption under pressure, and are marketed in steel cylinders and tank cars as a gas supply for rural homes and villages and as chemical raw materials for such derivatives as nitro-paraffins, chloro-paraffins, and acetone. The separation and utilization of natural gasoline, or *casinghead* gasoline as it is often called, are taken up under petroleum products in Chap. XXXVII.

After necessary purification, as will be described, the natural gas is compressed and sent through the distribution mains which network the country, being recompressed at periodic distances by gas engines. This natural gas is employed as fuel in many cities 1,000 miles or more from the producing wells. For peak demands it has proved economical to pipe natural gas in off-peak periods and liquefy it (−250°F.). Cleveland is thus proceeding, having installed three cork-insulated spherical tanks to hold each 600,000 gal. of liquefied gas equivalent to 50,000,000 cu. ft. of free gas.[1] However this important petroleum product is becoming increasingly essential as a chemical raw material for the manufacture of methanol and for obtaining hydrogen.[2]

Fuel Gas Purification.—In addition to the industrially valuable propane and butane, the raw natural gas also contains undesirable water and hydrogen sulfide which must be removed before it can be placed in the transmission lines. *Such purification is also practiced on other fuel gases.* There are four important methods employed for the dehydration of gas: compression, treatment with drying substances, adsorption, and refrigeration. The plant for water removal by *compression* consists of a gas compressor followed by a cooling system to remove the water vapor by condensation. The treatment of gas with *drying* substances has found widespread usage in this country. The most prominent agents for this purpose are sulfuric acid, glycerine, and concentrated solutions of calcium chloride or sodium thiocyanate. Plants of this type usually require a packed tower for the countercurrent treatment of the gas with the reagent, together with an evaporator for reconcentrating the dehydrating agents. The substance most widely mentioned as an *adsorption* medium for water in gases is silica gel. It will adsorb up to 40 per cent of its weight of moisture without increasing in volume and can easily be regenerated by heating. Gas may also be dehydrated by passing it over *refrigerated* coils. In general, this method is more costly than the others but, where exhaust steam is available to operate the refrigeration cycle, costs of refrigeration can be reduced. If the water occurring in most fuel gas is not removed, an unduly high corrosion will occur in the transmission lines, and trouble may also be had from the freezing of valves in cold weather.

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[1] MILLER and CLARK, Liquefying Natural Gas for Peak Load Supply, *Chem. & Met. Eng.*, **48**, No. 1, 74 (1941). Note: A disastrous fire occurred here in 1944.

[2] ADAMS, The Future of Natural Gas and Its Derivatives, *Chem. Eng. News*, **21**, 964 (1943).

The necessity of *removing* hydrogen sulfide[1] and other sulfides from gas is rather obvious, not only because of the corrosion problem but because the oxides of sulfur formed during combustion would be a nuisance to gas consumers. Also the sulfur compounds, particularly H_2S and S, have commercial value and are employed as a source of SO_2 for sulfuric acid plants. The sulfur can be obtained in a particularly valuable, finely precipitated form very suitable for an insecticide (see Chap. XIX for sulfur and its uses).

In raw fuel gases, except for some natural gases, the amount of hydrogen sulfide present may range from about 100 grains per 100 cu. ft. in blue gas to several hundred grains per 100 cu. ft. in coke-oven and coal gas, up to several thousand grains per 100 cu. ft. for refinery gas from sulfur crudes and natural gas from the sulfur-bearing regions. Other sulfur compounds may be present also. The various methods for sulfur removal may be best divided into the dry and wet methods.

The *dry method* used almost exclusively at the present time is the so-called *iron oxide*[2] *purification* process. It consists in the removal of sulfides by passing the gas through a series of boxes filled with iron oxide and wood shavings. Here reactions such as the following take place:

$$Fe_2O_3 \cdot xH_2O + 3H_2S \rightarrow Fe_2S_3 + (x + 3)H_2O$$

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[1] POWELL, Recovery of Sulfur from Fuel Gases, *Ind. Eng. Chem.*, **31**, 789 (1939); HOLLINGS, Removal of Sulfur Compounds from Gas, *Gas World*, **107**, 379–383, 471–476, 563 (1937); PERRY, *op. cit.*, p. 2362.

[2] PERRY, *op. cit.*, p. 2369.

The boxes should be interconnected in such a way that each can be shut off from the line at certain intervals for removal of used-up filler. This is either discarded or revivified by moistening and spreading out to obtain contact with air, thus allowing the sulfide to be changed back to the oxide.

$$2Fe_2S_3 + 3O_2 + xH_2O \rightarrow 2Fe_2O_3 \cdot xH_2O + 6S$$

Whereas this dry iron oxide or hydroxide process was widely employed in the United States prior to the First World War, it has been partly superseded by the wet processes. In Germany the spent and reactivated hydroxide is extracted by carbon disulfide for recovery of the sulfur. About three-quarters of the 50,000 metric tons of sulfur obtained in Germany in 1938 from gas purification came from this extraction.

There are numerous disadvantages connected with dry purification which may be partly or completely overcome by use of the *wet methods.* These are cost of materials employed, attention required, labor involved, cost of apparatus, and saving in needed space. The first liquid purification process to be widely used was the *Seaboard process.*[1] Here the purification is effected by scrubbing the gas with a dilute (3 per cent) solution of sodium carbonate. This treatment removes all of the hydrogen sulfide present, as well as any hydrogen cyanide and some of the carbon dioxide.

$$H_2S + Na_2CO_3 \rightleftarrows NaHS + NaHCO_3 \quad (1)$$
$$CO_2 + Na_2CO_3 + H_2O \rightleftarrows 2NaHCO_3 \quad (2)$$
$$HCN + Na_2CO_3 \rightleftarrows NaCN + NaHCO_3 \quad (3)$$

The fouled solution may be reactivated by blowing with air, reversing the above reactions. The standard equipment for this process is a packed or bubble-cap tower built in two separate sections or two separate towers, the fresh solution being sprayed down to meet the incoming gas in the upper section and air being blown upward countercurrently to the fouled solution in the lower section. Here the hydrogen sulfide is not recovered, being largely diluted with the air used in the activator, though sometimes the discharged air is piped to a boiler to furnish air for combustion. However the "extreme simplicity and economy inherent in this process account for its popularity, it having been installed in some sixty locations for the treatment of natural, refinery, coal, and water gas."[2]

Another important wet method is the *iron sulfur* or *Ferrox* recovery process. In this and the following sulfur-removal methods, the sulfur is recovered as such or as pure hydrogen sulfide which can be commercially utilized. In the Ferrox procedure the incoming gas is put through an absorber where a dilute (1 to 2 per cent) soda-ash solution with ferric hydroxide in suspension removes the sulfur impurities. The liquid flows to the "thionizer" where it is aerated, causing free sulfur to separate. This sulfur can be floated off, leaving the original solution revivified. The nickel sulfur recovery process is very similar to this except that the circulating sodium carbonate solution contains nickel as a reagent instead of iron. The hydrogen sulfide is absorbed as iron or nickel sulfide which is changed to sulfur. The reactions may be summarized as

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[1] Powell, *op. cit.;* Jacobsen, New Processes Aid in Manufacturing Clean Gas, *Chem. & Met. Eng.*, **36**, 588 (1929).

[2] Koppers Company, Koppers Seaboard Gas-purification Process, *Circ.* E-7704.

$$2H_2S + O_2 \rightarrow 2H_2O + 2S$$

The *Thylox*[1] process (Fig. 1) is the most extensively used wet method in American practice where elemental sulfur is recovered. It is applicable to low-sulfur gas of all kinds. The reagent starts with an aqueous solution of arsenious oxide (about 7 grams per liter) in soda ash. The main reactions are

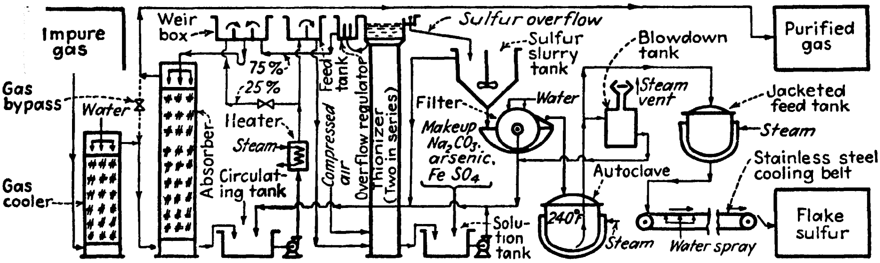

FIG. 1.—Gas purification by Koppers' Thylox process.

Absorption:

$$Na_4As_2S_5O_2 + H_2S \rightarrow Na_4As_2S_6O + H_2O$$

Regeneration:

$$Na_4As_2S_6O + \tfrac{1}{2}O_2 \rightarrow Na_4As_2S_5O_2 + S$$

A recent development in this field is the *amine absorption process* as exemplified by that using diethanolamine, marketed as the Girbotol process and developed by the Girdler[2] Corporation of Louisville, Ky. Another absorption process using sodium phenolate is shown in Fig. 2, which illustrates the type of equipment used. The Girbotol process is based on the principle that cold solutions of various organic amines have

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[1] POWELL, *op. cit.*

[2] ANON., Removal of Hydrogen Sulfide (flow sheet with description and pictures), *Chem. & Met. Eng.*, **47**, No. 1, 37, 1940; BOTTOMS, U.S. Pat., reissue 18,958 (1933); REED and WOOD, Recent Design Developments in Amine Gas Purification Plants, *Trans. Am. Inst. Chem. Engrs.*, **37**, 363 (1941).

TABLE 3.—GIRBOTOL ABSORPTION PROCESS[a]

	Plant A, high-sulfur refinery gas	Plant B, low-sulfur refinery gas near its dew point	Plant C, natural gas purification	Plant D, natural gas purification and dehydration
Gas rate, million standard cu. ft. per day	4.59	5.28	8.00	10.55
Gas temperature, °F	90	155	74	61
Absorber pressure, lb. per sq. in	100	290	400	400
Apparent inlet H_2S content, grains per 100 standard cu. ft[b]	2188	304	163	135
Apparent outlet H_2S content, grains per 100 standard cu. ft[b]	80	9		
Actual outlet H_2S content, grains per 100 standard cu. ft	11	......	0	0
Solution rate, gal. per min	75	21.4	22.5	13.4
Amine content of solution, per cent	9.5[c]	13.5[c]	5.0[d]	11.1[d]
H_2S content of lean solution, grains per gal	35	16	34	8
H_2S content of rich solution, grains per gal	910	586	492	847
Steam for reactivation, lb. per hr	2860	606	......	785
Pounds of steam per lb. of H_2S removed	4.8	6.6	......	9.2
Reboiler steam pressure, lb. per sq. in	7	10	7	37
Reactivator pressure, lb. per sq. in	2	6	1	1
Temperature of solution entering absorber, °F.	88	140	93	78
Temperature of solution leaving absorber, °F.	89	149	82	60
Temperature of solution entering reactivator, °F	195	206	176	194
Temperature of solution leaving reactivator, °F	223	232	215	265
Amine make-up, lb per day[e]	7	15	......	1
Dew point lowering, °F	......	......	......	35

[a] STARRS, Cost of Hydrogen Sulfide Removal from Refinery and Sour Natural Gases, *Ind. Eng. Chem., News Ed.*, **31**, 627 (1939).

[b] Including mercaptans.

[c] Per cent diethanolamine by weight.

[d] Per cent monoethanolamine by weight.

[e] Total losses including vaporization, chemical and mechanical, over a measurable period.

the ability to dissolve large volumes of such acidic gases as H_2S and CO_2. The particular absorbing liquid used for H_2S is diethanolamine in approximately 50 per cent aqueous solution. If dehydration is simultaneously desired, some of the water is replaced with ethylene glycol. If CO_2 is to be absorbed (see Chap. VIII), monoethanolamine is the preferred amine. The apparatus consists of a bubble-cap absorption tower, a bubble-cap stripping tower, and various pumps, condensers, and heat exchangers. The fouled liquid from the absorber passes through the heat exchangers to the stripper where it meets rising steam, is heated to about 250°F., and has its content of H_2S and other gases removed. The engineering aspects are presented in Table 3. Starrs[1] points out that the total cost of such purification "ranges from less than 0.5 cent per 1,000 standard cubic feet for natural gas with low hydrogen sulfide content to 2 cents per 1,000 standard cubic feet for refinery gas with unusually high hydrogen sulfide concentrations."

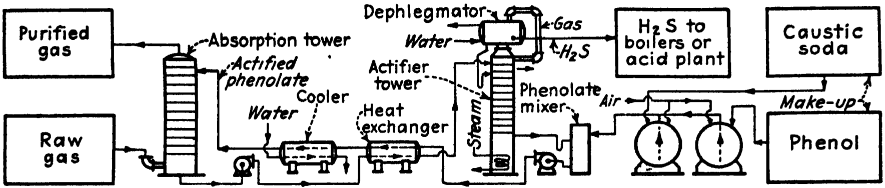

FIG. 2.—Gas purification flowsheet for Koppers' sodium phenolate process. See Table 6 for quantities.

The *sodium phenolate absorption* process employs a fairly concentrated solution of phenol in caustic soda and proceeds according to the following reaction,[2] reversed by steam heat:

$$\underset{\text{Sodium phenolate}}{NaOC_6H_5} + H_2S \rightleftarrows NaSH + \underset{\text{Phenol}}{C_6H_5OH}$$

TABLE 4.—OPERATING COSTS OF SEABOARD PROCESS[a]

Kind of gas	Refinery-still or natural gas
Capacity of plant	5,000,000 cu. ft. per day (normal temperature and pressure)
Sulfur content	1,000 grains H_2S per 100 cu. ft.
Sulfur removal	98 per cent
Gas pressure	60 lb. per sq. in. gage

	Per day
Labor: 6 hr. at $1 per hr	$ 6.00
Power: 1,000 kw.-hr. at 1 cent	10 00
Soda ash: 400 lb. at 1.2 cents	4.80
Maintenance	1 00
Total operating cost per day	$21.80
Cost per 1,000 cu. ft. of gas	0.436 cent

[a] DUNSTAN, *et al.*, "The Science of Petroleum," (Powell) p. 1806, Oxford University Press, New York, 1938.

This procedure in its industrial application involves the chemical or *unit process* of double decomposition and the *unit operations* of absorption and heat transfer. These are exemplified in Fig. 2. For this and practically all the other purification procedures described in this chapter, the absorp-

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[1] STARRS, Cost of Hydrogen Sulfide Removal from Refinery and Sour Natural Gases, *Ind. Eng. Chem., News Ed.*, Table 2, **31**, 627 (1939).

[2] POWELL, *op. cit.;* a typical phenolate solution contains 3 mols NaOH (120 grams per liter) and 2 mols phenol (188 grams per liter), *Private Communication.*

Table 5.—Operating Costs of Thylox Process[a]

Kind of gas	Refinery-still or natural gas
Capacity of plant	5,000,000 cu. ft. per day (normal temperature and pressure)
Sulfur content	1,000 grains H_2S per 100 cu. ft.
Sulfur removal	98 per cent
Gas pressure	60 lb. per sq. in. gage

	Per day
Labor: 12 hr. at $1 per hr	$12.00
Power: 1,200 kw.-hr. at 1 cent	12.00
Steam: 15,000 lb. at 30 cents per 1,000 lb	4.50
Soda ash: 600 lb. at 1.2 cents	7.20
Arsenious oxide: 150 lb. at 4 cents	6.00
Maintenance	2.00
Total operating cost per day	$43.70
Credit for recovered sulfur: 3 tons at $15	$45.00
Net operating credit per day	$ 1.30
Net credit per 1,000 cu. ft. of gas	0.026 cent

[a] Dunstan, *et al.*, "The Science of Petroleum" (Powell), p. 1807, Oxford University Press, New York, 1938.

Table 6.—Operating Costs of Phenolate Process[a]

Kind of gas	Refinery-still or natural
Capacity of plant	5,000,000 cu. ft. per day (normal temperature and pressure)
Sulfur content	1,000 grains H_2S per 100 cu. ft.
Sulfur removal	90 per cent
Gas pressure	60 lb. per sq. in. gage

	Per day
Labor: 6 hr. at $1 per hr	$ 6.00
Power: 37 kw.-hr. at 1 cent	0.37
Steam: 50,000 lb. at 30 cents per 1,000 lb	15.00
Water: 148,000 gal. at 1½ cents per 1,000 gal	2.22
Soda ash: 25 lb. at 1.2 cents	0.30
Crude tar acid: 50 lb. at 10 cents	5.00
Maintenance	2.00
Total operating cost per day (without credits)	$30.89
Cost per 1,000 cu. ft. of gas (without credits)	0.618 cent
Credits:	
Recovered H_2S: 3 tons at $15	$45.00
Steam from combustion of H_2S, 70 per cent boiler efficiency, 24,000 lb. at 30 cents per 1,000 lb	7.20
Total credits	$52.20
Net operating profit (with credits)	$21 31
Operating profit per 1,000 cu. ft. of gas (with credits)	0.426 cent

[a] Dunstan, *et al.*, "The Science of Petroleum" (Powell), p. 1808, Oxford University Press, New York, 1938.

tion[1] and its reverse or "activation," are carried out in bubble-cap or packed towers, constructed of steel and cast iron or occasionally, where intermittent operation is practiced, of stainless steel. The principles of a bubble-cap tower are shown by Fig. 5 and explained by Perry.[1] The phenolate purification furnishes an almost pure H_2S, of which more than 25,000 annual tons of sulfur equivalent are being recovered from 55,000,000 cu. ft. of fuel gas per day, and furnishing approximately 75,000 annual tons of 66°Bé. sulfuric acid.[2]

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[1] Perry, *op. cit.*, Absorption, Theory and Equipment, pp. 1138–1212; Furnas, Review of the Principles of Gas Scrubbing, *Gas Age-Record*, **80**, No. 8, 77–79 (1937).

COAL GAS

The processes for the distillation of coal are discussed in Chap. VI. Here will be given merely an outline of the treatment of the gas obtained from the distillation. Such gases come either from retorts or more usually from by-product coke ovens. The by-products in the hydraulic main first go via the foul main through a primary condenser and a baffled tar extractor as shown in Fig. 3 of Chap. VI, where the coal gas[3] is separated from the ammonia liquor and the coal tar. The gas has its ammonia removed as ammonium sulfate by bubbling through sulfuric acid in a lead-lined saturator. The coal-tar products such as benzene, toluene, and some naphthalene are scrubbed by straw oil in a packed light-oil tower or scrubber. The final steps of sulfur purification are similar to those described above under Natural Gas. The uses of coal gas are also parallel to those of natural gas.

WATER GAS (BLUE GAS)

Water gas,[4] often called *blue gas* because of the color of the flame when it is burned, finds important usage as a heating gas for coke ovens and as a low B.t.u. gas for reducing natural or coal gas. After mixing with oil gas, carbureted water gas results, which is widely sold for domestic consumption. Blue gas also serves as a step in making hydrogen (see page 128). The production of water gas is carried out by the reaction[5] of steam on incandescent coke or coal at a temperature around 1000°C. and higher where the rate and equilibrium are favorable, according to the principal equation:

$$\text{C (amorph.)} + H_2O(g) \rightarrow CO + H_2; \qquad \Delta H = +70{,}000 \text{ B.t.u. or } +38{,}900 \text{ cal.}^{6}$$

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[1] *Op. cit.*, pp. 1448–1457, 1436*ff.*, 1166, 1207.

[2] CRAISE and BROWN, Oil Refinery Hydrogen-sulfide Found to Be Economical Sulfuric Acid Source, *Chem. & Met. Eng.*, **44**, 376 (1937).

[3] Operating results on coal gas are given in Table 34, p. 2396, of Perry, *op. cit.*

[4] PERRY, *op. cit.*, pp. 2359, 2389–2396. See p. 2390 particularly for discussion of efficiencies, heat losses, heat, and material balances.

[5] PARKER, A Thermal Study of the Process of Manufacture of Water Gas, *J. Soc. Chem. Ind.*, **46**, 72T (1927); SCOTT, Mechanism of the Steam Carbon Reaction, *Ind. Eng. Chem.*, **33**, 1279–1285 (1941). For rate and equilibrium results, see Fulweiler, pp. 617–619, in "Rogers' Manual of Industrial Chemistry," 6th ed., D. Van Nostrand Company, Inc., New York, 1942

[6] PERRY, *op. cit.*, p. 718; on pp. 2386–2387 based on $H_2O(l)$, hence larger figures.

This reaction also occurs, apparently at several hundred degrees lower temperature:

$$C\ (\text{amorph.}) + 2H_2O(g) \rightarrow CO_2 + 2H_2; \qquad \Delta H = +34{,}200\ \text{B.t.u. or } +19{,}000\ \text{cal.}$$

These reactions are endothermic and, therefore, tend to cool off the coke bed rather rapidly, thus necessitating alternate "run" and "blow" periods. During the run period, the foregoing blue gas reactions take place, and salable or *make* gas results; during the blow period, air is introduced and ordinary combustion ensues, thus reheating the coke to incandescence and supplying the B.t.u.'s required by the endothermic useful gas-making reactions plus the various heat losses of the system. The reactions are

$$C\ (\text{amorph.}) + O_2 \rightarrow CO_2; \qquad \Delta H = -173{,}700\ \text{B.t.u. or } -96{,}500\ \text{cal.}$$
$$CO_2 + C\ (\text{amorph.}) \rightarrow 2CO; \qquad \Delta H = +69{,}800\ \text{B.t.u. or } +38{,}750\ \text{cal.}$$

The generator itself consists of a steel shell lined with a refractory as depicted in Fig. 3. It has doors at the top and bottom for the addition of fuel and the removal of ash. Air for blow or blasting enters at the grate level, and there is provision for the entrance of steam and the removal of gas at both the top and the bottom. The usual cycle is of 4 to 6 min. in length, of which 25 per cent should be blow for usual operation. The run period is generally split into "uprun" and "downrun" periods. In such, the first part is usually an uprun with the steam being admitted at the bottom and the gas being removed at the top; this is then reversed to a downrun and finally reversed again to give sufficient uprun to clear the ashpit of gas just before the blow. The ratio of uprun to downrun varies considerably with type of fuel. Materials[1] used in making 1,000 cu. ft. of water gas from coke are coke, dry, 34.7 lb.; air for blast, 2,230 cu. ft.; steam, 51.9 lb.

For city gas, where it is desired to enhance[2] the heating value of water gas, oil is atomized into the hot blue gas. A plant producing this *carbureted blue gas* has, in addition to the ordinary generator, a carburetor and a superheater as shown in Fig. 3. These are also large refractory-lined steel shells with brick checkerwork, at least in the superheater. The combustion gases formed during the blow period serve to heat the arches, side walls, and the checkerwork. Then during the run, oil is sprayed into the carburetor, is cracked or pyrolyzed, and is passed on mixed with the water gas. In most cases it is necessary to have tar

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[1] MORRIS, *Proc. Tech. Sessions, Amer. Gas Assoc.*, **1922**, 21–52.

[2] VITTINGHOFF, The Manufacture of High B.t.u. Carbureted Water Gas, *Gas Age*, **81**, No. 12, 23–26, 31 (1938).

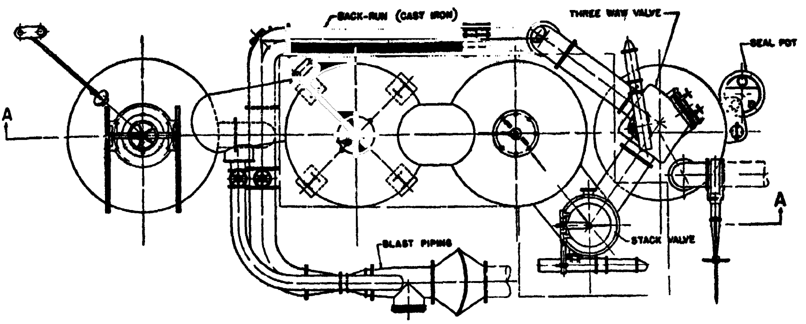
TABLE 7.—BREAKDOWN OF FOUR-MINUTE CYCLE ON REVERSE-FLOW CARBURETED WATER-GAS MACHINE OF FIG. 3[a]
(Fuel is bituminous coal)

Operation	Per cent	Seconds	Detail
Blow............	30	72	Primary air is admitted at base of generator and passes up through fuel bed for the purpose of bringing the carbon up to gas-making temperature. Secondary air is admitted into the large connection between the generator and carburetor to complete combustion of blast gases. This heats, to the highest temperature, the arches in lower part of carburetor. The blast gases pass up the carburetor, down the superheater, and up and out the stack, losing much of their heat to the brickwork as they pass.
Blowrun...	5	12	The function of the blowrun, which is used generally when bituminous coal is the generator fuel, is to recover as much of the volatiles from the coal as possible and to prevent overheating of the carburetor and superheater. This blowrun is usually carried on immediately after the blow when the fire is at its highest temperature and the blast gases contain the highest per cent of CO, and volatiles from the coal are passing off at a high rate. The blowrun is accomplished by closing the secondary air valve and the stack valve and allowing this mixture of coal gas and producer gas to pass through the machine and into the washbox and out to the holder as make gas. Usually the blowrun is longer after a fresh fuel charge has been put in the generator, the length of the blowrun being decreased each run until a new charge is made.
Uprun...........	30	72	Steam is admitted at the base of the generator and passes up through the red-hot coke or coal, forming blue gas. Oil spraying into the carburetor begins 5 sec. after start of uprun, thus causing all oil cracking to take place in an atmosphere of blue gas. Oil gas is formed by the pyrolysis of the oil entering countercurrent into the uprising hot blue gas and from heat of radiation. The blue and oil gases mix and pass on to the superheater where the pyrolysis of the gasified oil is continued and the gases fixed (or made permanent).
Backrun.........	33	79	This replaces the old downrun as steam is now admitted in the bottom of superheater, passing up the superheater where it is heated, down the carburetor, reacting with the red-hot carbon on the carburetor arches deposited from oil cracking, further reacting with coal or carbon in generator, finally passing out of the bottom of generator directly through the cast-iron backrun pipe through the three-way valve into the wash-box. Sometimes additional oil is sprayed into top of generator during this backrun to supply carbon for main blue gas reaction if oil is cheaper than coal, and also to furnish more low-gravity oil gas (rich in hydrogen) particularly when employing a high percentage of blowrun in the make gas.
Final uprun......	2	5	This short uprun makes a purge unnecessary. It puts a blanket of steam between the blue gas in base of generator and the air that follows. This leaves carburetor and superheater filled with backrun steam to be exhausted to atmosphere.

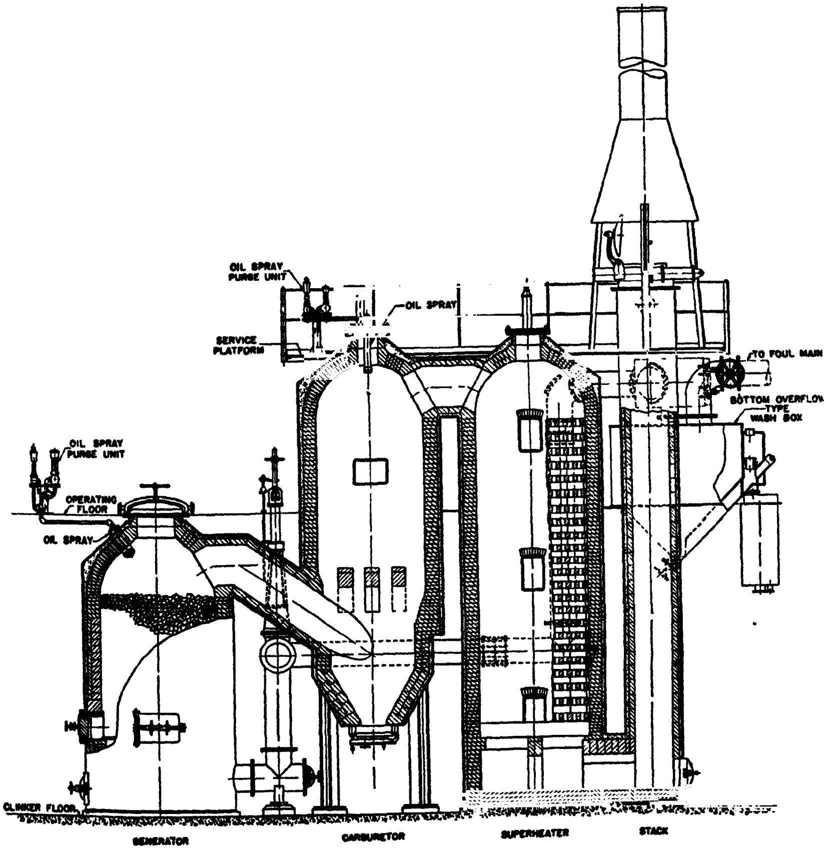
[a] DORMER, Experience with Nine-foot Reverse Flow Water Gas Machine, Mid-West Gas Association School, Iowa State College, Ames, Iowa, September, 1941; *Private Communication* from Semet-Solvay Engineering Corp.

traps to remove the heavy water-gas tar formed during the vaporization of the oil.

One of the newer installations producing 520 to 540 B.t.u. per cu. ft. of gas, using 23 to 25 lb. of coal and 2.7 to 3.1 gal. of heavy oil per



PLAN VIEW



ELEVATION - SECTION A-A

Fig. 3.—Reverse-flow water-gas machine for light or heavy oil operation. (*Courtesy of Semet-Solvay Engineering Corporation.*)

M cu. ft. (1,000 cu. ft.), is detailed in Fig. 3 and Table 7. This is the modern answer to the demand for economically manufactured gas for city consumption wherein the use of low-priced bituminous coal and heavy oils is efficient. The carburetor is *not* filled with checkerwork but is provided with arches only; thus, a source of trouble is avoided when heavy petroleum oils are used which fill up and block checkerwork with the coke formed and reduce the heat transfer. The plant of Fig. 3 is called a *reverse-flow* water-gas machine because the usual flow of gas through the carburetor and superheater is reversed by elevating the carburetor somewhat and changing the flues. This causes better pyrolysis of the carburetor oil as it is sprayed in countercurrent to the hot blue gas and permits the use of cheaper, heavier oils; this also results in better heat balance and lessened repairs from carbon blocks or stoppages.

PRODUCER GAS[1]

The original producer gas was made by passing air through a thick bed of hot fuel to give the over-all reaction:

$$2C \text{ (amorph.)} + O_2 \rightarrow 2CO; \qquad \Delta H = -104{,}000 \text{ B.t.u. or } -57{,}800 \text{ cal.}$$

Complete combustion takes place where the air enters.

$$C \text{ (amorph.)} + O_2 \rightarrow CO_2; \qquad \Delta H = -173{,}700 \text{ B.t.u. or } -96{,}500 \text{ cal.}$$

The carbon dioxide reacts with the hot carbon forming carbon monoxide.[2]

$$C \text{ (amorph.)} + CO_2 \rightarrow 2CO; \qquad \Delta H = +69{,}750 \text{ B.t.u. or } +38{,}750 \text{ cal.}$$

It is now common practice to admit steam along with the air entering a producer. The primary purpose of this is to use up as much as possible of the exothermic energy from the reaction between carbon and oxygen to supply the endothermic reaction between carbon and steam. Also, this endothermic water-gas reaction reduces the temperature to the point where the ash is not fused to a clinker that is troublesome to remove. The most desirable amount of steam to use is sometimes given as 25 to 30 per cent of the weight of coke involved in the reaction. The three main points observed in designing and operating a producer are (1) the exposed fuel surface should be large and kept uniform, (2) the time of contact between gas and fuel should be as long as possible, (3) the temperature should be as high as economical.

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[1] PERRY, *op. cit.*, pp. 2361, 2386–2389.

[2] Equilibrium and rate conditions for these reactions are given by Fulweiler, *op. cit.*, p. 737.

Producers are usually large, refractory-lined or water-jacketed steel shells with a gas outlet and fuel distributor at the top and a steam-air tuyère inlet and ash-removal system at the bottom. A modern gas producer is shown in Fig. 4. Here the firebrick lining has been superseded by a heavy steel inner wall with a water jacket. This prevents side wall clinker and also furnishes hot water or steam at 5 lb. pressure for mixing with the air. Figure 4 depicts a rotating grate for continuous ash removal and for helping to maintain the even distribution of the coke. In operating a producer, either a regenerator or a recuperator should be

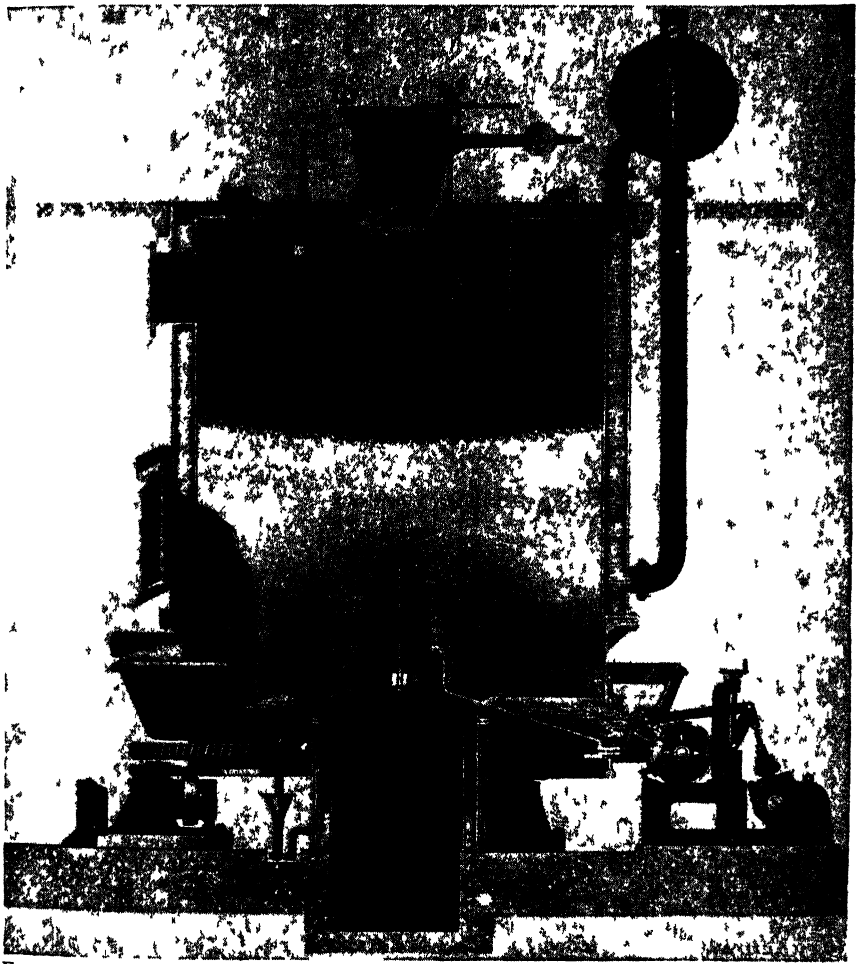

Fig. 4.—Typical arrangement of the Semet-Solvay Koller type gas producer when gasifying coke or anthracite coal

used to transfer the heat from the outgoing gases to the incoming air. A regenerator recovers heat by alternate passing of the hot and cold gases through a checkerwork, while a recuperator operates by the continuous passage of the two gases through adjacent flues. For both producer-gas and water-gas plants, a waste-heat boiler is a valuable adjunct.

Producer gas is a cheap, low-B.t.u. fuel gas used for all types of industrial heating purposes near where the gas is generated, a prime example being its application to heat coke ovens and other furnaces. The producer-gas reaction also serves as one of the basic reactions in making ammonia (see Chap. XX).

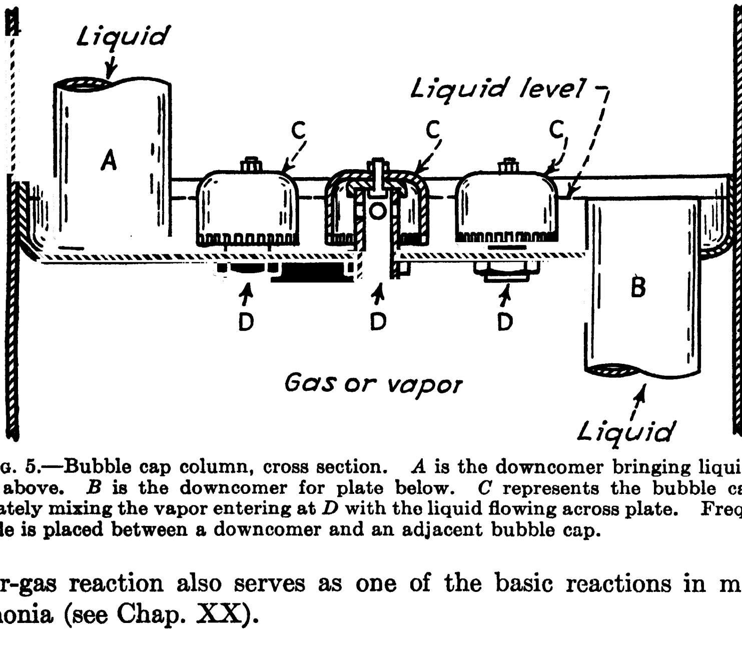

Fig. 5.—Bubble cap column, cross section. *A* is the downcomer bringing liquid from plate above. *B* is the downcomer for plate below. *C* represents the bubble caps for intimately mixing the vapor entering at *D* with the liquid flowing across plate. Frequently a baffle is placed between a downcomer and an adjacent bubble cap.

Problems

1. A large three-lift water-sealed gas holder used for the storage of city gas is to be removed from service for internal inspection. State the principal precautions you would observe to ensure safety.

2. A producer gas has the following composition: CO, 24.0 per cent; CO_2, 4.0 per cent; O_2, 2.0 per cent; N_2, 70 per cent. Calculate

a. The cubic feet of gas at 70°F. and 750 mm. Hg pressure, per pound of carbon present.

b. The volume of air at the conditions of part (*a*), required for the combustion of 100 cu. ft. of the gas at the same conditions if it is desired that the total O_2 content present before combustion shall be 20 per cent in excess of that theoretically required.

c. The percentage composition by volume of the gases leaving the burner of part (*b*), assuming complete combustion.

d. The volume of the gases leaving the combustion of parts (*b*) and (*c*) at a temperature of 600°F. and a pressure of 750 mm. Hg per 100 cu. ft. of gas burned.

3. *Using van der Waals' equation of state, calculate the density of methane at 500 lb. per sq. in. abs. and 80°F.*

4. The reaction for the production of blue water gas containing 48 per cent H_2, 42 per cent CO, 5 per cent CO_2, and 5 per cent N_2 is presumed to be

$$C + H_2O \rightarrow CO + H_2.$$

a. Using handbook data, compute the heat absorbed in the production of the actual blue water gas, per pound of carbon consumed. Assume that the reaction takes place at 20°C.

b. How much heat would be absorbed per pound of carbon consumed if the reaction took place at 1000°C?

5. A natural gas has the composition CH_4, 93 per cent; N_2, 4 per cent; H_2, 2 per cent; O_2, 1 per cent. The gas is piped from the well at a temperature of 16°C. and a pressure of 40 lb. per sq. in. abs. Assuming that the simple gas law is applicable, calculate

a. The partial pressure of the O_2.

b. The partial volume of N_2 per 20 cu. ft. of gas.

c. The density of the mixture in pounds per cubic foot at the existing conditions.

6. A gas with a heating value of 1950 B.t.u. per cu. ft. has the following composition: C_2H_4 and C_6H_6, 55.1 per cent; O_2, 1.3 per cent; CH_4, 15.5 per cent; C_2H_6, 25.0 per cent; N_2, 3.1 per cent. Calculate the percentage of C_2H_4 and C_6H_6.

7. Calculate the theoretical flame temperature of the following gas when burned with theoretical amount of air. Combustion is only 75 per cent complete. Air and gas are initially at a temperature of 18°C.

CO, 20 per cent; N_2, 74 per cent; CO_2, 6 per cent.

8. Calculate the number of calories required to heat, from 373 to 2000°C., 10,000 cu. ft. (s.t.p.) of a gas having the following composition (by volume): CO_2, 19 per cent; O_2, 2 per cent; N_2, 79 per cent.

9. A producer gas (8 per cent CO_2, 17 per cent H_2, 26 per cent CO, 1 per cent CH_4, 48 per cent N_2) is made from a coal containing 72 per cent C, 4 per cent H_2O, 7 per cent ash, 17 per cent volatile combustibles. Assuming that all steam and water are decomposed and the volatile combustibles contain only C and H, calculate

a. Cubic feet of producer gas (dry s.t.p.) per pound of coal fired.

b. Cubic feet of air used (dry s.t.p.) per pound of coal fired.

c. Pounds of steam decomposed per pound of coal fired.

d. Ultimate analysis of the fuel.

e. Pounds of steam decomposed per pound of coal fired in excess of that brought in by the fuel itself.

10. A producer gas analyzing 3.6 per cent CO_2, 0.8 per cent C_2H_4, 2.7 per cent CH_4, 11.6 per cent H_2, 29.7 per cent CO_2, and 51.6 per cent N_2 under a positive pressure of 1.5 in. of water and saturated with water vapor at 100°F. is burned in a furnace with air which enters at 70°F. and 60 per cent saturated with water vapor. The flue gas, which is at 460°F., analyzes 8.1 per cent CO_2, 1.7 per cent CO, 7.9 per cent O_2, and 82.3 per cent N_2. The barometer is 747 mm. Calculate

a. Percentage of excess air.

b. Cubic feet of gas formed per cubic foot of fuel gas entering.

c. Cubic feet of air supplied per cubic foot of fuel gas entering.

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CHAPTER VIII

INDUSTRIAL GASES

The industrial gases are important for many specific uses. As a class they have already become among the most vital raw materials for the chemical industry. Every day, new uses are being developed by aggressive researchers and trained sales personnel of the manufacturing companies.

CARBON DIOXIDE

Carbon dioxide in liquid and solid forms has been known for over a century. Although Thilorier produced solid carbon dioxide in 1834 from the liquid material, it was not until about 1925 that the solid product was exploited commercially.[1] Now the daily productive capacity has been estimated in excess of 1,100 tons of solid[2] and about 1,500 tons per day for both solid and liquid. The annual production of liquid and gaseous carbon dioxide in 1943 was 280,348,000 lb. For solid carbon dioxide the output was 505,609,000 lb.[3]

Uses[4] and Economics.—The beverage industry consumes about 90 per cent of the liquid carbon dioxide for carbonation and the ice cream industry about 90 per cent of the solid form. Other uses for solid carbon dioxide include shrink-fitting of machine parts, hardening fancy forms of ice cream, and chilling rubber goods for easy and accurate trimming. The liquid is used in fire protection, as an explosive for coal mining, in cleaning water wells, as a respiratory stimulant, as an insecticide, and for many other purposes. Gaseous carbon dioxide from the burning of limestone and the calcination of sodium bicarbonate forms one of the raw materials for soda ash (see page 278). Carbon dioxide is also used in the manufacture of white lead and of salicylic acid (from sodium phenate by the Kolbe synthesis).

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[1] REICH, Solid CO_2, Technology Defers to Distribution Problems, *Chem. & Met. Eng.*, **38**, 270 (1931).

[2] MARTIN, Dry Ice from Ordinary Flue Gases, *Refrig. Eng.*, **34**, 219 (1937); LONGAKER, The Chemical Uses and Methods of Handling Solid and Liquid Carbon Dioxide, *Chem. Industries*, **52**, 210 (1943).

[3] See *Chem. & Met. Eng.*, **51**, No. 2, 129 (1944).

[4] JONES, Carbon Dioxide in Industry, *Chem. & Met. Eng.*, **40**, 76 (1933). This includes an excellent chart showing uses. HUNT, Solid CO_2, *Refrig. Eng.*, **35**, 83 (1938).

Carbon dioxide has advantages over ordinary acids for neutralizing alkalies because it is easily shipped in solid form, is noncorrosive in nature, and is light in weight. Chemically it is equivalent to more than twice its shipping weight in sulfuric acid or about five times its weight in hydrochloric acid. In respect to food refrigeration, solid carbon dioxide is primarily a transport refrigerant. Its advantages cannot be attributed to any one single factor but result from its dryness, its relatively high specific gravity, its excellent refrigerating effect, its low temperature, and the insulating and desiccating action of the gas evolved. In some instances it is possible to substitute 1 lb. of solid carbon dioxide for as much as 15 to 20 lb. of water ice, although more often 3 to 6 lb. of water ice is replaced. For example, a railway refrigerator car going from coast to coast is charged with 8,000 to 11,000 lb. of ice and must have some of it replaced at least twice. This nonpaying load usually totals 18,000 lb. and takes up about one tenth of the volume of the car. With a car insulated with 7-in. insulation and a gasproof steel shell, one charging of 3,000 lb. of solid carbon dioxide is sufficient for from 6 to 15 days, and the refrigerant takes up only a little room. The temperature difference between the top and the bottom of a well-designed car will be only about 3°F.

The cost of production of solid carbon dioxide in existing plants of over 20 tons per day capacity has been divided as follows:

	Delivered Cost of Dry Ice, Per Cent
Power and/or fuel	30
Labor (including maintenance)	10
Chemical supplies	8
Depreciation and taxes	22
Delivery expense (plus losses)	30

Manufacture of Pure CO_2.—Various manufacturing systems for carbon dioxide operate on two classes of crude gas—either those containing 18 per cent of CO_2 or occasionally about twice as much (limekiln[1] gas), and those containing 99 per cent of carbon dioxide, both, however, contaminated with slight impurities which must be removed. An absorption system is used for concentrating this 18 per cent CO_2 gas up to over 99 per cent. In all cases the almost pure carbon dioxide must be given

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[1] Orr, Byproduct CO_2 Builds a New Refrigerant Business, *Chem. & Met. Eng.*, **40**, 250 (1933). This article describes CO_2 from kiln gas to solid CO_2 using Carba procedure. Diagram of press and flow sheet are included. Anon., Carbon Dioxide from Lime Kiln Gases, *Chem. & Met. Eng.*, **46**, 97 (1939). Pictured flow sheet is given.

TABLE 1.—COMPARISON OF PHYSICAL PROPERTIES OF SOLID CO_2 AND WATER ICE

	Solid CO_2	Water ice
Specific gravity	1.56	1.00
Sublimation point or melting point	−109.6°F.	32°F.
Critical temperature	88.43°F.	689°F.
Critical pressure	1,071 lb. abs.	2,860.6 lb. abs. at 32°F.
Latent heat of fusion, lb	82.0 B.t.u.	144 B.t.u.
Latent heat of vaporization, lb	158.6 B.t.u.	1,074.29 B.t.u. at 2°F.
Weight of gas, cu. ft	0.117 lb.	0.000304 lb.
Weight solid, cu. ft	90 lb.	57 lb.
Latent heat of sublimation, lb	248 B.t.u.	
Refrigerating effect, lb	275 B.t.u.	144 B.t.u.

various chemical treatments for the removal of the minor impurities which contaminate the gas. The reaction[1] for the concentration of the carbon dioxide is

$$Na_2CO_3 + CO_2 + H_2O \rightleftarrows 2NaHCO_3$$

This reaction is forced to the right by increasing the partial pressure of the CO_2 and by reducing the temperature. It is forced to the left by heating up the sodium bicarbonate solution. The absorption efficiency of 18 per cent CO_2 is not very good as the quantities of Fig. 1 indicate. This absorption could be increased by use of another absorbing tower. However the CO_2 available in this case comes from the combustion of carbon in a boiler plant generating the required steam; it happens that the steam is the critical, expensive, and controlling item. To carry out this manufacture, the principal *unit operations* (Op.) and *unit processes* (Pr.) that are necessary are detailed in the following tabulation:

Coke or other carbonaceous fuel burned, giving heat for steam and economizer, and furnishing 18 per cent CO_2 (Pr. and Op.).

Gas purified, cooled, and washed (Op.).

Gas reacted countercurrent forming $NaHCO_3$ solution from CO_2 and Na_2CO_3 solution (Pr.).

Concentrated (99.9 per cent) CO_2 boiled out of $NaHCO_3$ solution (Pr. and Op.).

CO_2 purified and dried (Pr.).

CO_2 compressed, cooled, and liquefied (Op.).

For "Dry Ice":

Liquid CO_2 subjected to reduction in pressure with consequent partial solidification (Op.).

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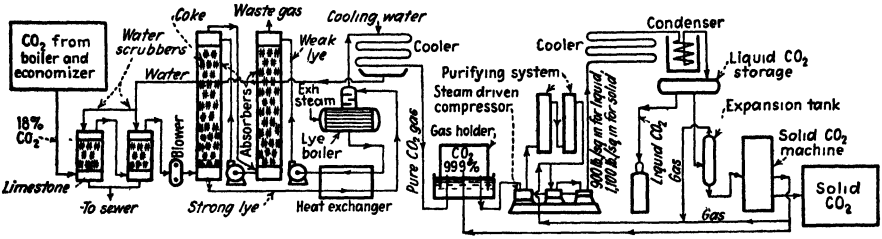
[1] PERRY, *op. cit.*, pp. 1133–1138. Here are given equations for the partial pressure of CO_2 together with references to original work. *Cf.* Gas Absorption in PERRY, *op. cit.*, pp. 1138*ff.*, particularly pp. 1174 and 1189. SHERWOOD, "Absorption and Extraction," pp. 205–220, McGraw-Hill Book Company, Inc., New York, 1937.

Recirculation, with recompression and recooling of evaporated CO_2 (Op.).
CO_2 "snow" compressed to solid cake (Op.).
Dry Ice cakes sawed to shape (Op.).

A typical flow sheet, continuously producing either liquid or solid and embracing the sequences of these unit operations and unit processes, is shown in Fig. 1. In the merchandising of liquid carbon dioxide, the energy (and hence expense) involved in handling the cylinders, full and empty, is so great that this one fact has required the installation of many relatively small plants economically located in consuming centers. However, bulk shipment of relatively low-pressure liquid *cold*[1] carbon dioxide is now being practiced to save container cost and weight. Where pure carbon dioxide from fermentation, for example, is not available, the practice, largely conditioned by the energy balance, is to burn coke to furnish the necessary energy and the carbon dioxide at the same time. If heat exchangers are properly designed, it is necessary to buy but little outside energy for solid CO_2 and none for liquid CO_2 (see Fig. 1), the live steam generated by the coke boilers being sufficient to furnish power for pumping and compression, while the exhaust steam from steam-driven compressors will boil off the carbon dioxide from the sodium bicarbonate solution in the lye boiler. These coke plants are splendid examples of well-balanced energy and chemical requirements. It takes an efficiently designed coke boiler to generate 20,000 lb. of steam from 1 ton of coke, but this is the actual experience of the better plants. The temperature of combustion is so high in these special coke boilers when operated to furnish an 18 per cent CO_2 gas, that it has been economical to employ expensive but more serviceable carborundum bricks for the boiler setting.



Coke* 10
Cooling H_2O (total) = 20,000 gallons
Lye makeup (Na_2CO_3) = 25 pounds
Steam = 20,000 pounds
Electricity (total) = 10 kw-hr
Labor = 8 man-hr
Required to produce 1 ton of solid CO_2 from 18 per cent flue gas

*In place of 1 ton coke some plants use 1 ton soft coal 130 gal fuel oil or 2,200 cu.ft natural gas

FIG. 1.—Flow sheet for CO_2 (solid or liquid) from coke.

In following Fig. 1, it should be observed that after the coke is burned in the boiler, producing 18 per cent CO_2, these hot gases pass through an economizer and then to the limestone water scrubbers where the gases are further cooled and the SO_2 and dust removed. In the meanwhile the "strong lye" (solution of $NaHCO_3$), after being warmed in the heat exchanger, is further warmed in the economizer (not shown in Fig. 1) before passing to the lye boiler where the $NaHCO_3$ is decomposed back to Na_2CO_3 by being boiled (about 245°F.) with the exhaust steam from the CO_2 compressors.

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[1] GETZ and GUERTZ, Transportation and Storage of Bulk Low-pressure Liquid Carbon Dioxide, *Ind. Eng. Chem.*, **33**, 1124 (1941).

The concentrated (99.9 per cent) gas escapes through a rectifying section connected to the lye boiler body where it comes in contact with the entering hot strong lye from the economizer and the heat exchanger. The temperature of the entering lye is raised while the temperature of the gas is reduced. The gas is passed to a water cooler where the temperature is lowered further and the water vapor content is greatly reduced. The condensate from the cooler returns to the weak lye circuit. The gas is collected in a gas holder.

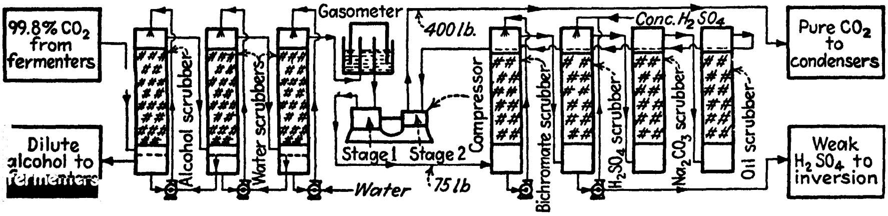
From the gas holder the CO_2 passes to a purifying system, consisting of an oil separator and a scrubber containing $KMnO_4$ or $K_2Cr_2O_7$ solution which oxidizes organic impurities that would affect the taste. In the second purifying scrubber sulfuric acid or calcium chloride dries the gas.

The completely deodorized gas is compressed in a three-stage compressor driven by live steam from the coke boiler and delivering exhaust steam to the lye boiler. The first stage raises the pressure to 80 lb.; the second, to 400 lb.; and the third, to 900 lb., or to 1,100 lb. if solid CO_2 is desired. During compression, care should be taken to have very good cooling because the gas leaving the compressor is above its critical temperature of 88.43°F. Therefore, it is passed first through a cooler and next to the liquefier which is connected with the filling stand. The gas charged into the cylinders as a liquid has a purity of at least 99.9 per cent, will not contain 0.1 per cent moisture, and is free of organic impurities.

The equipment used is almost all of steel, though the water limestone scrubbers are sometimes lined with concrete to lessen attack by aqueous sulfite. The absorbers are tall steel towers, 100 ft. high with frequently placed steel platforms on which porous coke is supported to ensure good contact with the rising gases.

A very large source of carbon dioxide is the *fermentation* industry as described in Chap. XXXI. If yeast is used, alcohol and CO_2 are produced, while certain other microorganisms generate solvents and a gaseous mixture of H_2 and CO_2. The yield of CO_2 varies with the mode of fermentation. From starchy material, such as corn, there is obtained from 1 bushel, for example, 2½ gal. cf 190-proof ethyl alcohol and 17 lb. CO_2. The recovery and purification of CO_2 from fermentation differ from the absorption system, in that the temperature seldom exceeds 105°F., so that no special cooling is necessary and the CO_2 content of the gas starts usually above 99.5 per cent. When the fermenters are sealed for the recovery of the gases, a purer and higher yield of carbon dioxide per gallon of mash is obtained and the yield of alcohol is increased by at least 1 per cent by alcohol recovery from the CO_2 scrubbers.

A typical CO_2 recovery from fermentation follows the procedure of Reich[1] as illustrated in the flow sheet of Fig. 2. Here the purification consists of an oxidation of the organic impurities and a dehydration by means of chemicals in liquid form. The gas from the fermenters is passed through three scrubbers containing stoneware spiral packing and on to the gasometer. The first scrubber contains a weak alcoholic solution which acts as a preliminary purifier and removes most of the alcohol carried in the gas. The next two scrubbers, in which the scrubbing medium is deaerated water, removes almost all the water-soluble impurities. The scrubbing liquid is pumped either to the stills or to the fermenters for alcohol recovery.



Bichromate	0.5 lb.	Water	2,000 gal.	Per ton solid CO_2
Sodium carbonate	0.01 lb.	Electricity	5.4 kw.-hr.+	
Oil	0.01 gal.	Direct labor	0.2 man-hr.	
H_2SO_4 (66°Bé.)	6 gal.*			

* Weak H_2SO_4 all recovered for use in molasses fermentation
+ Not including solid CO_2 compressing system

FIG. 2.—Flow sheet for fermentation CO_2 purification—Reich process.

From the gasometer the gas is conducted to a scrubber containing $K_2Cr_2O_7$ solution which oxidizes the aldehydes and alcohols in the gas. In the second scrubber which contains sulfuric acid the oxidation is completed and the gas is dehydrated. The carbon dioxide leaving the acid scrubber contains some entrained acid which is removed in a tower filled with coke and over which a Na_2CO_3 solution is circulated. When the acid is neutralized, carbon dioxide is released. Before going to the compressor, the gas passes through a scrubber containing a small amount of glycerine which absorbs the oxidized products and delivers an odorless gas to the compressor. The sulfuric acid, after being used for deodorization and drying, is pumped to the distillery where it serves for the pH control in molasses fermentation.

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[1] REICH, Liquid CO_2—How Technology Has Harnessed Available Sources, *Chem. & Met. Eng.*, **38**, 136 (1931); REICH, Solid CO_2, Technology Defers to Distribution Problems, *Chem. & Met. Eng.*, **38**, 270 (1931). These articles include fundamental data, flow sheets, and temperatures of several processes.

There are a number of other methods for purifying carbon dioxide. Among them mention should be made of the *silica gel* process[1] wherein water and odors are removed from the partly compressed gas (80 lb.) by adsorption and the silica gel revivified by heated air. The Backhaus[2] process employs activated carbon for similar purposes but works on the uncompressed gas. The carbon is regenerated by heating with direct and indirect steam and finally dried by hot air.

Other *absorbing liquids* in addition to a soda ash solution are employed. Potassium carbonate offers slight advantages but it costs more than soda ash. However, still more expensive absorbents, namely, amino alcohols, are being used competitively because of their greater power to absorb CO_2 and the easier reversibility of this absorption. In particular is *monoethanolamine*[3] of industrial importance, because of its high rate of absorption for CO_2. It is being employed as a 10 to 20 per cent aqueous solution.

Aqueous solutions of monoethanolamine are used for the absorption of CO_2 from combustion gases as a step in making liquid CO_2; however, in a special case, an aqueous solution of diethanolamine is selected where CO_2 is to be removed in conjunction with H_2S. In some instances, solutions of monoethanolamine and ethylene glycol function to remove CO_2 and dehydrate the gases simultaneously.

Several factors determine the concentration of solutions of monoethanolamine. The more dilute the solution, the lower the evaporation and the mechanical losses. In most cases, the gases at atmospheric pressure are scrubbed in absorber towers packed with steel turnings, coke, or Raschig rings. Under these conditions a 10 to 15-per cent monoethanolamine solution will be concentrated enough to strip the CO_2 completely out of a combustion gas containing 12 to 15 per cent CO_2 when the minimum circulation rate necessary for good scrubbing is maintained. With this solution the quantity of CO_2 liberated per gallon of solution circulated, when scrubbing a gas at atmospheric pressure and temperature with about 15 per cent of CO_2, will be about 0.20 to 0.25 lb. The CO_2 is not completely removed from monoethanolamine solutions in commercial installations on boiling at atmospheric pressure, and the residual CO_2 content after reactivation amounts to about 0.012 lb. of CO_2 per gallon for each per cent of monoethanolamine present in the solution. By raising the operating pressure to about 40 lb. gage pressure in order to increase the reactivator temperature to 140 or 145°C., this residual CO_2 can be almost completely removed from the monoethanolamine solutions by the effect of the higher temperature in dissociating the monoethanolamine carbonate. Under such conditions, net CO_2 removal rates as high as 0.88 lb. per gal. of solution have been obtained.[1]

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[1] REICH, Liquid CO_2—How Technology Has Harnessed the Available Sources, *Chem. & Met. Eng.*, **38**, 140 (1931).

[2] REICH, *ibid.*, p. 139.

[3] MASON and DODGE, Equilibrium Absorption of Carbon Dioxide by Solutions of the Ethanolamines, *Trans. Am. Inst. Chem. Engrs.*, **32**, 27 (1936). *Cf.* PERRY, *op. cit.*, pp. 1133–1137. This is the Girbotol process of the Girdler Corp. See Chap. VII under Fuel Gas Purification.

With soda ash solutions under ordinary conditions the recovery will be from one-half to two-thirds of the 0.20 to 0.25 lb. mentioned above with the added necessity of using four or five times as much scrubbing contact between the flue gas and the soda ash solution and with more steam required for stripping the CO_2 from the solution. Less absorbing capacity is required for the amine than for sodium carbonate, but the recovery is the same in either case in a properly designed plant. It is possible to reduce the carbon dioxide in the exit gases to 1 per cent, but it is not always economical to do this.

The monoethanolamine solutions used for removing CO_2 from hydrogen are usually more concentrated than those used for recovering CO_2 from flue gases. The hydrogen is generally scrubbed at elevated pressures (up to about 250 lb. gage), which proportionately reduces amine vaporization losses. Since bubble plate absorbers are mostly employed, a wide range of solution circulation rates may be used. The CO_2 content of the hydrogen is usually fairly high (18 to 33 per cent), giving conditions that are favorable for high absorption capacities. In these plants the solution strength usually is kept between 20 and 30 per cent amine and the CO_2 liberated amounts to 0.35 to 0.40 lb. per gal. of solution circulated. This rate of CO_2 removal is obtained when the absorption is carried out so that the purified hydrogen will contain less than 0.1 per cent of CO_2.

At the present, one objection to the use of ethanolamine solutions is their corrosiveness due to their oxidation to glycine and oxalic acid, both compounds being corrosive to iron. The monoethanolamine is much less susceptible to oxidation than the di- and tri-compounds. Although usually all that is necessary is the continuous redistillation of a portion of the solution (discarding the residue), at times the entire solution has to be discarded and a new one made up. If a redistillation unit is used, it may be connected in series with the main regeneration unit; then the steam used for redistillation of the solution may be utilized in stripping CO_2 from the solution in the regeneration equipment.

Solid carbon dioxide is manufactured from the liquid, as outlined in Figs. 1 and 2. The compression installation however frequently employs two sets of compressors. The primary compressors are three- or four-stage machines which compress the gas from the gasometer to the operating pressure of about 1,100 lb. The return, or backblow gases, from the presses and the expansion bottles are recompressed in the two stages of the secondary compressors to the working pressure of 1,100 lb. The gas from the four-stage primary compressor is passed through a water cooler and condensed, flowing as liquid CO_2 to the liquid storage. As required for the presses, liquid is drawn from an expansion tank where the pressure is partly released (to 560 lb.) in order to accomplish preliminary cooling of the liquid (to 32°F.). The yield is increased from 25 to 50 per cent by precooling the liquid. The released gas passes to the two-stage secondary compressor where it is recompressed to the 1,100 lb. working pressure for recooling and recondensing. Liquid CO_2 from the expansion tank is then expanded through a nozzle into the press, provided with top and bottom rams.

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[1] *Private Communication* from the Girdler Corporation. For plant, see pictured flow sheet in *Chem. & Met. Eng.*, **47**, 32 (1940).

The cycle of operation of the press is very simple. With the upper ram at the top and the lower ram closing the bottom of the expansion chamber, liquid CO_2 is admitted for a predetermined time until sufficient snow has formed. During this period, gas formed from expansion is conducted from the expansion chamber to the secondary compressors. The liquid feed is then cut off, and the residual pressure in the expansion chamber is released to the gasometer. When this is done, the upper ram is lowered to compact the snow to a dense cake which has a specific gravity of about 1.5. The upper ram is raised and then the lower ram, on which rests the finished block, is lowered. The block is discharged and sent to the cutting tables and then to packing and storage. Occasionally for solid CO_2, special purification is practiced on the partly compressed CO_2 by washing with $KMnO_4$ solution followed by a drying tower with either calcium chloride or sulfuric acid.

HYDROGEN

Uses and Economics.—Hydrogen is used in modern industry for a great many applications. Table 2 gives an estimate for certain specified consumptions. However, a very extensive use to which hydrogen is put is for the hydrogenation of oils, the so-called *hardening process*, which is described in Chap. XXVIII. Over 400,000 tons of hydrogenated oil are produced in the United States yearly, this having increased from 275,000 tons in 1934. The amount of hydrogen required for the hydrogenation reaction varies greatly as Table 3 shows. In addition to these chemical applications, hydrogen is very widely employed for welding and other heating processes. For such purposes the hydrogen is supplied in the form of a compressed gas in cylinders. The U.S. Census reports some 40 establishments scattered throughout the United States, selling over a million M cu. ft. of such compressed hydrogen for nearly $2,000,000.

TABLE 2.—ESTIMATED HYDROGEN CONSUMPTION OF THE UNITED STATES IN 1939 FOR AMMONIA, METHANOL, ISOOCTANE, AND PETROLEUM HYDROGENATION[a]

	Production	H_2 consumed (1,000,000 cu. ft.)
Synthetic ammonia	200,000 tons	16,800
Synthetic methanol	34,255,699 gal.	7,880
Technical isooctane	1,500,000 bbl.	2,400
Petroleum hydrogenation	9 plants producing 1,500,000 bbl. aviation and special gasolines by hydrogenation	7,000
Total		34,080

[a] STENGEL and SHREVE, Economic Aspects of Hydrogenation, *Ind. Eng. Chem.*, **32**, 1212–1215 (1940). The production of all these products has been greatly increased by the demands of the Second World War.

TABLE 3.—HYDROGEN REQUIRED FOR TYPICAL PRODUCTS[a]

Raw material	Product	Hydrogen required, cu. ft., 60°F., per ton of product
Phenol	Cyclohexanol	25,000
Naphthalene	Tetralin	12,000
Olein	Stearin	2,600
Diisobutylene	Isooctane	6,700

[a] STENGEL and SHREVE, Economic Aspects of Hydrogenation, *Ind. Eng. Chem.*, **32**, 1212–1215 (1940).

Not included in these census figures are the large quantities of hydrogen made and consumed in plants where hydrogenation[1] is practiced.

HYDROGEN MANUFACTURE

Prior to 1900, the uses of hydrogen were few, and the supply was filled almost entirely by electrolytic processes. Since then, the demand for large-scale hydrogen production for chemical reactions, both inorganic and organic, has increased rapidly and there are now available the following important methods for manufacture:

1. Electrolysis of water.
2. By-product from electrolysis of aqueous sodium chloride (*cf.* Chap. XV).
3. Steam-iron method.

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[1] An excellent presentation of the unit process of hydrogenation together with cost for producing hydrogen by different procedures is given by Fenske in his chapter on Hydrogenation in the book edited by Groggins "Unit Processes in Organic Synthesis," 2d ed., McGraw-Hill Book Company, Inc., New York, 1938. *Cf.* STENGEL and SHREVE, Economic Aspects of Hydrogenation, *Ind. Eng. Chem.*, **32**, 1212–1215 (1940); TAYLOR, "Industrial Hydrogen," Reinhold Publishing Corporation, New York, 1921.

4. Water gas-catalytic process.
5. Liquefaction of nonhydrogen constituents of fuel gas (water gas, coal, or refinery gas).
6. Thermal cracking of hydrocarbons such as natural gas.
7. Action of steam on natural or refinery gases.
8. Cracking of ammonia.
9. By-product from butanol fermentation (*cf.* Chap. XXXI).

The particular process to be used in any installation depends on the cost of power, the amount of hydrogen desired, and the purity required. For a small unit, hydrogen can be produced easiest electrolytically, particularly where cheap electricity is available. For a large plant, many factors have to be considered, such as amount and nature of impurities. For example, a synthetic ammonia plant might use the water gas-catalytic process which is cheap and where admixture with nitrogen is desirable. On the other hand, a plant hydrogenating vegetable oils requires very pure hydrogen so as not to impart any objectionable taste and usually employs the steam on heated iron method. However, each year sees some improvement in gas purification procedures, thus widening the application of the cruder gases like hydrogen from coal and hydrocarbons.

Electrolytic Method.—The electrolytic process consists in passing direct current through a dilute aqueous solution of alkali, decomposing the water according to the following equation:

$$2H_2O(l) \rightarrow 2H_2 + O_2; \qquad \Delta H = +136{,}700 \text{ cal.}$$

The theoretical decomposition voltage for this electrolysis is 1.23 volts at room temperature; however, owing to overvoltage of hydrogen on the electrodes and also to cell resistance itself, voltages of 2 or more volts are actually required. A typical commercial[1] cell electrolyzes a 15 per cent NaOH solution, uses an iron cathode and a nickel-plated iron anode, has an asbestos diaphragm[2] separating the electrode compartments, and operates at temperatures from 60 to 70°C. The nickel plating of the anode reduces the oxygen overvoltage. Most types of cells produce about 7.0 cu. ft. (9.408 cu. ft. theoretically) of hydrogen and half as much oxygen per kilowatt-hour, the gas being around 99.7 per cent pure and being suitable even for hydrogenation of edible oils. The cells are of two types: the filter press type, where each plate is an individual cell, and the unit cell type, usually containing two anode compartments with a cathode compartment between them. In most installations, the oxygen produced is wasted unless it can be used right at the plant.

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[1] MANTELL, "Industrial Electrochemistry," 2d ed., McGraw-Hill Book Company, Inc., New York, 1940; PERRY, *op. cit.*, pp. 2766–2768 gives operating data for the Knowles and the Levin cells; KNOWLES, Hydrogen Plant at Warfield Works, Canada, *J. Soc. Chem. Ind.*, **51**, 355 (1932). This plant electrolyzes 25 per cent KOH solution.

[2] PERRY, *op. cit.*, p. 2768.

Steam-iron Method.[1]—Hydrogen is produced by the steam-iron method by passing excess steam over iron heated to about 650°C., the reaction proceeding according to the equation:

$$3\text{Fe} + 4\text{H}_2\text{O}(g) \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2; \qquad \Delta H = -38{,}800 \text{ cal.}$$

This is a reversible reaction with the production of hydrogen being favored by the excess steam and at as low a temperature as practical. Patents were taken out on this process as early as 1861, but it was not until about 1900 that it was successfully developed. The commercial reactions are carried out in retorts filled with spongy iron, a large exposed surface being a vital factor in the operation. The periods of passing steam up through the iron (10 min.) are alternated with those during which blue water gas is passed downward (20 min.), reducing the iron oxide back to iron at around 650°C.

$$\text{Fe}_3\text{O}_4 + 2\text{CO} + 2\text{H}_2 \rightarrow 3\text{Fe} + 2\text{CO}_2 + 2\text{H}_2\text{O}(g); \qquad \Delta H = +16{,}000 \text{ cal.}$$

The spent water gas is then burned around the retorts to heat them, providing the calories needed by this endothermic reaction. This process of hydrogen production is economical for medium-sized installations and gives very pure hydrogen (99 per cent or higher); thus, it finds widespread use in plants hydrogenating edible oils.

Water-gas Catalytic Process.—If water gas (one volume) and steam (three volumes) are mixed, heated to 450 to 500°C., and passed over a suitable catalyst, usually iron oxide promoted with chromium oxide, hydrogen is produced:

$$\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftarrows \text{H}_2(g) + \text{CO}_2(g); \qquad \Delta H = -9{,}800 \text{ cal.}$$

This reaction is carried on in presence of some initial hydrogen and of excess steam needed to force reaction to the right. Efficient heat exchangers must be employed to transfer the sensible heat of the gases leaving the catalyst chamber to the incoming gases. The CO_2 contained in the water gas and that formed amounting to from 20 to 40 per cent are removed by scrubbing with water at 25 to 30 atm., while any residual CO may be dissolved out by washing at 200 atm. with an ammoniacal solution of a cuprous salt. This catalytic water gas or Bosch process has been used for the largest establishments requiring hydrogen, namely the large synthetic ammonia plants (Chap. XX). The raw materials are coal to give the coke used, steam and air to make blue water gas (Chap. VII), together with more steam for the change from carbon monoxide to carbon dioxide and hydrogen. The purity of the hydrogen produced in the past was not sufficient for hydrogenation of fats, but improved purification methods are now available.

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[1] TAYLOR, *op. cit.*, p. 25.

The fundamental equilibrium may be expressed:[1]

$$K = \frac{p\text{CO} \times p\text{H}_2\text{O}}{p\text{CO}_2 \times p\text{H}_2}$$

where $K = 0.15$ for 500°C., 0.32 for 600°C., and 0.58 for 700°C. Based on reaction at 500°C., using a catalyst to increase the rate and ending with a volume ratio of 2.5 to 1 for steam to hydrogen in equilibrium gases, then

$$K \text{ at } 500°\text{C.} = \frac{p\text{CO}}{p\text{CO}_2} \times \frac{p\text{H}_2\text{O}}{p\text{H}_2} = \frac{p\text{CO}}{p\text{CO}_2} \times \frac{2.5}{1} = 0.15$$

whence $p\text{CO}/p\text{CO}_2$ under these conditions = 0.06, or in the exit gases the carbon monoxide will be 6 volume per cent of the carbon dioxide.

Liquefaction.—Hydrogen is produced from water gas or from coke-oven or cracking still gas by the liquefaction and removal of the other components. The process consists of the following steps: (1) H_2S removal by passing over iron oxide, (2) CO_2 removal by scrubbing with water or NaOH under pressure, (3) removal of CO and N_2 by liquefaction. This latter step is accomplished in three stages: (1) ammonia refrigeration to −35°C., (2) cooling effect upon vaporization of CO-rich liquid removed from previously treated gases, (3) cooling by liquid air to −205°C. Hydrogen obtained by this method runs from 97 to 97.5 per cent pure. Although this liquefaction procedure has been employed in Europe, American chemical engineers have considered it too expensive.

Hydrogen from Natural Gas.—Hydrogen is produced from natural gas by thermal or "Thermatomic" decomposition.[2] The gas is passed over a heated brick checkerwork at a temperature of 1200°C. This serves to decompose the gas into carbon black and hydrogen, both valuable products (see Chap. IX).

$$\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2; \qquad \Delta H = +20{,}300 \text{ cal.}$$

This by-product hydrogen is probably one of the cheapest sources of hydrogen available. At one time it was burned as a fuel; it is now employed for ammonia synthesis.

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[1] TAYLOR, *op. cit.*, p. 60.

[2] ANON., Carbon Black Production in the Monroe Gas Field, *Chem. & Met. Eng.*, **39**, 380 (1932).

Hydrogen may also be produced from natural gas[1] by its reaction with steam in the presence of an alumina base catalyst:

$$CH_4 + H_2O \rightarrow CO + 3H_2; \qquad \Delta H = +49{,}200 \text{ cal.}$$

More steam is added, and the catalytic water-gas reaction carried out over an iron base catalyst:

$$CO + H_2O(g) \rightarrow CO_2 + H_2; \qquad \Delta H = -9{,}800 \text{ cal.}$$

Summation: $$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

This change is carried out in two steps which allow both reactions to proceed under the optimum conditions. The reactions may be performed in one step with a reduction in yields. The CO_2 is scrubbed out by monoethanolamine or by water under pressure.[2] This procedure for making hydrogen is conducted in a continuous manner with the catalyst in tubes heated on the outside to supply the endothermic heat required. High-chromium-alloy steel is needed to withstand the temperature of the hydrocarbon-steam reaction. Although methane is given in this procedure, it is applicable to other hydrocarbons both paraffinic and olefinic, existing in the large quantities of gas available at the petroleum refineries. Consequently, these gases as well as natural gas are now being employed on a large scale to furnish hydrogen for ammonia and for the ordinary hydrogenations of petroleum products.

Cracked Ammonia.[3]—A recent development consists of the preparation of a mixture of nitrogen, 1 volume, and hydrogen, 3 volumes, from the cracking of ammonia. The process consists in vaporizing the liquid NH_3 from cylinders, heating it to 1600°F., passing it over an active catalyst, and then cooling it in heat exchangers where the incoming gas is vaporized. The cost of cracked ammonia, including power and amortization, is $4 per M cu. ft. Brandt states, "a single 150-lb. cylinder of anhydrous ammonia will produce 6,750 cu. ft. of cracked ammonia. This is equivalent to the contents of some 33 hydrogen cylinders." It is not economically feasible to separate the nitrogen and hydrogen from this process; however, almost pure nitrogen can be easily made by burning out the hydrogen. This nitrogen will cost about $3 per M cu. ft. as compared to $10 for pure nitrogen in cylinders. Cracked NH_3 gives too cold a flame to replace H_2 in oxyhydrogen torches. It has found widespread usage in the heat-treating of metals, however.

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[1] RAIGORODSKY and DOTTERWEICH, War Products from Natural Gas, *Petroleum Refiner*, **22**, 125 (1943), with chart of plant.

[2] SHERWOOD, "Absorption and Extraction," pp. 220–222, McGraw-Hill Book Company, Inc., New York, 1937.

[3] BRANDT, Cracked Ammonia, *Chem. Industries*, **68**, 186 (1941); BRANDT, Handling Ammonia for Metal Treatment, *Metals & Alloys*, **16**, No. 1, 60 (1942).

OXYGEN AND NITROGEN

Uses.—The most important use[1] of compressed gaseous or liquid *oxygen* is in oxyhydrogen and oxyacetylene torches for cutting and welding steel and for cleaning off mill scale before painting. But cheap oxygen or even an enriched air would be of great value in many reactions of combustion or oxidation both in the inorganic and organic fields, by saving part of the handling of the fourfold volume of nitrogen when air is employed. Liquid oxygen is also used to some extent as an explosive when mixed with powdered carbon. Oxygen is sold compressed to 2,000 lb. in cylinders[2] holding 110 or 220 cu. ft. at atmospheric pressure and 70°F., or as a liquid transported in freight cars in large double-walled tanks of steel with a high vacuum between the walls. *Nitrogen* for the synthesis of NH_3 is usually made from producer gas (*cf.* Chap. XX). Cylinder nitrogen is employed as a reagent in many instances, but it also finds use as an inert atmosphere where the presence of oxygen might be dangerous.

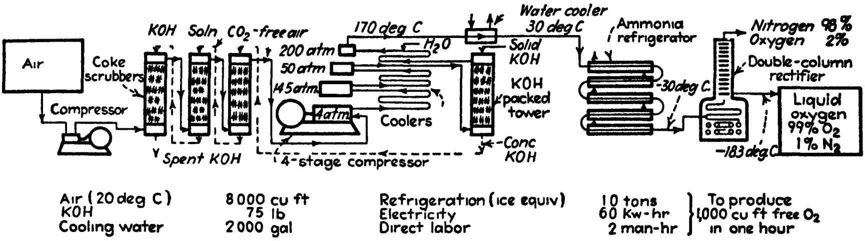

FIG. 3—Flow sheet for production of oxygen and nitrogen through liquefaction of air

TABLE 4.—COMPOSITION OF THE ATMOSPHERE[a]

Gas	Boiling point, °C.	Boiling point, °K	By volume	By weight
Nitrogen	−195 81	77 3	78 03 per cent	
Oxygen	−182 97	90 1	20 99 per cent	
Argon	−185 86	87 2	0 94 per cent	
Carbon dioxide	− 78 43	194 7	0 031 per cent	
Neon	−246 09	27 0	1 part in 65,000	1 lb in 44 tons
Helium.	−268 92	4 2	1 part in 200,000	1 lb. in 725 tons
Krypton	−153 23	119 9	1 part in 1,000,000	1 lb. in 173 tons
Xenon	−108 06	165 0	1 part in 11,000,000	1 lb. in 1,208 tons

[a] GROSS, Rare Gases in Everyday Use, *J. Chem. Education*, **18**, 533 (1941).

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[1] CARTER and REINHARD, Modern Uses of Oxygen, *J. Chem. Education*, **19**, 91 (1942).

[2] PERRY, *op. cit.*, pp. 2916–2917 lists some of the more important regulations for the handling of compressed gases in cylinders.

Manufacture.—Relatively pure oxygen and nitrogen are produced commercially from air[1] by a typical flow sheet as presented in Fig. 3. The composition of the atmosphere is given in Table 4. The air is first compressed, and the CO_2 and any dust present are removed by scrubbing with KOH solution. The air is further compressed to 200 atm. in four stages, with water cooling between each stage. Any moisture that condenses out during this operation is drawn off or is removed by passage through a tower packed with solid KOH or activated alumina. The gas coming from the fourth compression stage is at 170°C.; it is water-cooled to 10 to 30°C. and usually then further cooled to −30°C. by ammonia refrigeration. The air, at 200 atm. and −30°C., goes to a combined liquefier and separator, as shown roughly in Fig. 3 and in detail in Fig. 4. Here the purified, compressed, and cooled air is liquefied and separated into its constituents according to the following fundamental principles:

1. The interchange of heat in heat exchangers such as double pipe coils.
2. The adiabatic expansion of the compressed air to cool by the Joule-Thompson[2] effect, owing to energy being consumed in overcoming the attraction between the molecules.
3. The cooling of the compressed gases by allowing them to perform work (Claude modification). One kilo of air at 200 atm. and 10°C. when simply expanding to 5 atm. produces a cooling effect of 10 kg.-cal. (Joule-Thompson effect), while if the same quantity of air expands to 5 atm. in a cylinder *doing work*, the cooling effect is 23 kg.-cal., assuming that the working engine has an efficiency of 70 per cent.[3] This latter effects a cooling of 135°C.
4. The cooling of the liquids by evaporation.
5. The separation of liquid oxygen from the more volatile nitrogen in a bubble-cap column. Nitrogen boils at −195.8°C. and oxygen at −183°C. The difference of 12.8 deg. in boiling point permits a fractional separation of the two liquids, owing to the fundamental fact of any fractionation in a column that the more volatile will have a higher percentage in the vapor in equilibrium with a lower percentage of this constituent in the liquid.[4] Thus the repetition of these equilibriums, more or less perfect, constitutes the "plates" of the fractionating column and causes the more volatile or substantially pure nitrogen to come off at the top, while substantially pure oxygen is obtained at the bottom.

These principles are applied[5] in practice according to two systems:

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[1] PERRY, *op. cit.*, pp. 2626–2638. Outline is included of minimum work required to separate two gases by liquefaction (Dodge and Housem).

[2] *Ibid.*, pp. 477, 709. Although nitrogen and oxygen exhibit the Joule-Thompson effect, notable exceptions are hydrogen and helium.

[3] ANON, The Briey Liquid Oxygen Plant, *Engineering*, **140**, 135 (1935).

[4] PERRY, *op. cit.*, p. 1369, where vapor and liquid equilibriums are plotted.

[5] The principles involved here are presented by Ruheman, "The Separation of Gases," Oxford University Press, New York, 1940. Typical plants are described in

the Linde and the Claude. Both cool the compressed gas and depend upon a gradual or "self" lowering of the temperature by countercurrent cooling of the incoming gas against outgoing gas, to the air liquefaction temperature. The Linde system employs the Joule-Thompson effect for its critical cooling while the Claude system uses the Joule-Thompson cooling for only 30 per cent of the incoming air, the other 70 per cent being cooled by performing external work. In this latter case it is better not to cool the compressed air below −30°C., or the work to be performed, and hence the cooling, is lessened by the energy heatwise removed. After a liquefier is working, the operating pressure can usually be reduced to about 50 atm.

a. Entrance for compressed air at 200 atm.
b. Accumulated liquid rich in oxygen
c. Cooled and liquefied air entering lower column
d. Lower rectifying column
e. Exit valve for liquid, 40 ± per cent oxygen
f. Liquid entering upper column
g. Upper rectifying column
h. Accumulated oxygen liquid
i. Exit valve for oxygen, 99+ per cent pure
j. Condensing tubes and dome for lower column
k. Condensed overhead from lower column, rich in nitrogen
l. Release valve for flow to upper column
m. Heat exchanger, nitrogen-rich liquid to nitrogen gas
n. Nitrogen-rich liquid entering upper column
o. Cold gaseous nitrogen
p. Heat exchanger, entering air to leaving gaseous nitrogen

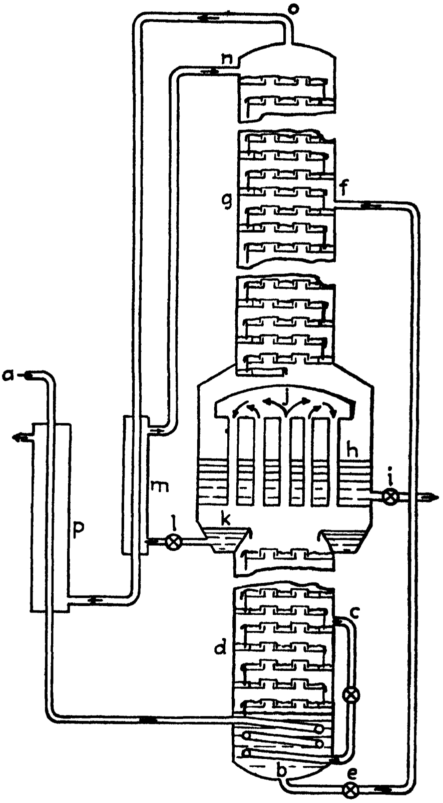

FIG. 4.—Diagram of Linde liquefier and double-column rectifier. This rectifier separates liquid air into the more volatile nitrogen (b.p. −195.8°C. or 77.3°K.) and the less volatile oxygen (b.p. −183°C. or 90.1°K.).

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the following articles: Anon., The Briey Liquid Oxygen Plant, *Engineering*, **140**, 135 (1935); Kuryla and Clevenger, Liquid Oxygen Explosives at Pachuca, *Am. Inst. Mining Met. Engrs.*, **69**, 271 (1923); also Perry, *op. cit.*, pp. 620, 2626–2637.

About 95 per cent[1] of the oxygen manufactured is obtained by the system developed by Carl von Linde in Germany around 1900. The heart of this system is the double-column liquefier and rectifier as shown in Fig. 4. The Claude system is slightly more complicated as it diverts 70 per cent of the high-pressure air to perform useful low compression of the incoming air and to cool itself simultaneously. This system is apparently more efficient and is meeting some modern acceptance.

The double-column equipment shown in Fig. 4 is actually constructed with its special heat exchangers, columns, and expansion valves all a part of one setup and encased in the same insulating covering. The cooled and compressed air enters countercurrent to the outgoing nitrogen through a heat exchanger. Although only one such exchanger is shown in the figure, it is common practice to install two. These are used alternately, so that, when one is plugged by ice from water that escaped previous removal, the air may be passed through the second. This permits removal of the ice without interrupting the procedure. The cold compressed air issuing from the heat exchanger (*p*) is still warmer than the liquid in the column; hence it is passed through the coil in the bottom of the column (*d*) and thus supplies the heat necessary for the vaporization in this lower section. This colder compressed air is finally expanded through valve (*c*) into the lower column (*d*) from initially 200 atm. and later on from 50 atm. down to 4 to 6 atm., being sufficiently cooled here through the Joule-Thompson effect to be liquefied. As a liquid, the air enters the lower section of the column and flows downward against the rising vapors of its more volatile constituent, nitrogen. As is true of any such fractionation, the less volatile constituent, oxygen, collects in the bottom at (*b*). Part is vaporized to carry on the rectification, but any accumulation of this liquid containing about 40 per cent oxygen is forced by the pressure drop between (*d*) at 4 to 6 atm. and (*g*) at 1.3 atm. (absolute), to pass through the valve (*e*) to the upper rectifying section, entering at (*f*). The 40 per cent liquid oxygen passes down the upper column losing its more volatile nitrogen until it accumulates at (*h*) as liquid oxygen of 99 and more per cent purity. Although some of this liquid oxygen boils off and thus renders latent the heat given off by the condensation of the nitrogen vapor at the higher pressure on the lower side of the dome at (*j*), much of it is drawn off through valve (*i*) into double-wall vacuum containers for storage or sale.

The nitrogen in the liquid air entering at (*c*), as the more volatile constituent gradually volatilizes, passes upward and is cooled and condensed by the tubes and dome of (*j*). The curved dome here deflects the drippings to the collector trough at (*k*) where a liquid quite rich in nitrogen collects. This nitrogen-rich liquid is moved to the top of the upper column by the prevailing pressure differential through the control valve (*l*), though some of this nitrogen-rich liquid spills off the trough to supply reflux liquid to the upper plates of column (*d*). The reason why the lower boiling nitrogen (−195.8°C. at 1 atm.) is liquefied by the higher boiling (−183°C. at 1 atm.) oxygen is because of the *higher* pressure on the liquid rich in nitrogen in the lower column. As the liquid rich in nitrogen goes to the upper column, it is cooled further by the gaseous nitrogen leaving the column at (*o*), in order that it will not evaporate too quickly when it enters this region of lower pressure. As the liquid rich in nitrogen passes down the plates of column (*g*), the more volatile nitrogen vapors are fractionated off, are washed fairly free of oxygen, and pass out of the top of the column as cold nitrogen vapor of around −195°C. This cold nitrogen as it leaves the apparatus is warmed in the heat exchangers (*m*) and (*p*).

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[1] Carter and Reinhard, *op. cit.*

RARE GASES OF THE ATMOSPHERE

The rare gases argon, neon, xenon, and krypton are obtained from the atmosphere.[1] These gases are separated by side take-off columns at various points in the double rectifying column such as is employed for obtaining oxygen and nitrogen from air, as depicted in Fig. 4. The krypton and xenon, having higher boiling points, are removed near the bottom of the lower column, the argon near the bottom of the upper column, and the neon and helium, having lower boiling points, from the top of the upper column (see Table 4).

One of the surprising developments of the past few years is the industrial consumption of these rare and chemically inert materials. Their utilization in the light industry is because they are *chemically* inert but possess very desirable *electrical* properties. Such usage is divided between the gas conductor tube lamps, the so-called "neon" lights, and the newly developed fluorescent lights.

The *gas conductor lamps* are largely sold in a form shaped to spell out various signs. These are of glass tubing with the electrodes sealed in each end and filled with the rare gases including helium or mixtures thereof, with or without mercury. The light is caused by the flow of the current which may be 25 milliamperes at 15,000 volts, with the light emission determined by the gas in the tube. Table 5 summarizes the commercial colors. The power consumption is low in comparison to that of incandescent lamps.

The *fluorescent tubes* are a startling and recent development and produce a soft nonglaring light under very economical conditions. They

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[1] Metzger, Traces from Tons, *Ind. Eng. Chem.*, **27**, 112 (1935); Gross, Rare Gases in Everyday Use, *J. Chem. Education*, **18**, 533 (1941), with diagram of side columns for separation of rare gases.

TABLE 5.—COMMERCIAL COLOR CHART FOR "NEON" LIGHTS[a]
(Clear or colored glass, uncoated)

Color	Gas	Pressure, mm.	Glass	Mercury
Deep red	Neon	10–18	Soft red	No
Red	Neon	10–18	Clear	No
Gold (yellow)	Helium	3– 4	Noviol (amber)	No
Light green	Argon-neon mixture[b]	10–20	Uranium (green)	Yes
Dark green	Argon-neon mixture[b]	10–20	Noviol (amber)	Yes
Light blue	Argon-neon mixture[b]	10–20	Clear	Yes
Dark blue	Argon-neon mixture[b]	10–20	Purple	Yes
White	Helium	3– 4	Clear	No

[a] GROSS, Rare Gases in Everyday Use, *J. Chem. Education*, **18**, 533 (1941).
[b] To meet extreme winter conditions, an argon-neon-helium mixture is substituted.

are filled with one of these rare gases and are provided with a fluorescent coating of a "phosphor" on the inside of the glass. The function of the latter is to supplement the visible light given out by the rare gas, by the transformation of the invisible or ultraviolet rays of the gas into those wave lengths visible to the human eye. This supplementary or "extra" light imparts a very pleasing effect. Table 6 presents some of these phosphor chemicals or fluorescent materials, which to give the proper clarity of transformed light must be of a purity that has never before been obtained in any chemicals of commerce. The resulting combination of light from the gases and the phosphor is presented in Table 7. These fluorescent lights as pointed out by Gross[1] have the following advantages:

TABLE 6.—FLUORESCENT CHEMICALS[a]

Phosphor	General Color Produced
Calcium tungstate	Blue
Magnesium tungstate	Blue-white
Zinc silicate	Green
Zinc beryllium silicate	Yellow-white
Cadmium silicate	Yellow-pink
Cadmium borate	Pink

[a] GROSS, Rare Gases in Everyday Use, *J. Chem. Education*, **18**, 537 (1941).

1. Brilliant colors of high luminosity.
2. Shaped or formed to any requirements of size, shape, or description.
3. Effectiveness and advertising attraction due to light emitted by entire volume of tube, not built up by spots of light.
4. High efficiency and low operating cost due to greater conversion of electrical energy to light.

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[1] GROSS, *op. cit.*, p. 537.

5. Long life.
6. Better adaptability to flashing due to instantaneous response to starting and stopping current flow.

Whereas the average 100-watt incandescent lamp emits 15.8 lumens per watt, these fluorescent lights furnish from 20 to 70 lumens per watt, with about 30 to 35 as an average for the performance of white and daylight colors.

TABLE 7.—FLUORESCENT TUBE COLOR CHART[a]
(Tubing coated with a phosphor)

Color	Gas	Pressure, mm.	Glass and coating
Rose pink	Neon	10–18	Clear blue
Gold	Neon-argon mixtures + mercury	10–20	Noviol yellow
Yellow	Neon	10–18	Clear green
Green	Neon-argon mixtures + mercury	10–20	Clear green
Blue	Neon-argon mixtures + mercury	10–20	Blue
White	Neon-argon mixtures + mercury	10–20	Clear white

[a] GROSS, Rare Gases in Everyday Use, *J. Chem. Education*, **18**, 537 (1941).

HELIUM

With the discovery of helium in certain Kansas[1] natural gases about 1900, the helium industry had its beginning. The first plants were constructed with the idea of supplying helium for the lighter-than-air airships of the Allies in the First World War. The present government-owned plant at Amarillo, Tex., was completed in 1929 and produces helium only as it is needed. The natural gas raw material comes out of the ground at a pressure of 700 lb. per sq. in. and contains about 1.75 per cent helium.

The first step in the helium process[2] is the removal of carbon dioxide that is present in amounts of around 0.5 per cent by volume. It is scrubbed out by a NaOH solution or by an ethanolamine solution at a pressure of 650 lb. per sq. in. The remainder of the gas is then cooled progressively to about −185°C. by countercurrent heat exchangers. At this temperature and a pressure of 300 lb. per sq. in., all the constituents of the natural gas except helium and a small amount of nitrogen are liquids, which are withdrawn from the system and used for cooling the incoming gases again. The helium is drawn off the top and sent to further purification. Here further cooling and separation give a final product of 98 per cent purity. The helium is shipped in long seamless steel cylinders at pressures of 2,000 lb. per sq. in. Since this plant has been in operation, it has produced 50,000,000 cu. ft. of helium at an average cost of $12 per M cu. ft.

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[1] CADY, Beginnings of the Helium Industry, *Ind. Eng. Chem.*, **30**, 845 (1938).

[2] BOTTOMS, Removing Acidic Gases by Reaction with Organic Bases, *Chem. & Met. Eng.*, **38**, 465 (1931); SEIBEL, Production of Helium at Amarillo, *Ind. Eng. Chem.*, **30**, 848 (1938). Pictures and excellent description.

The most important use for helium is in lighter-than-air aircraft, where it has replaced the very flammable hydrogen. It has 92.5 per cent of the lifting power of hydrogen. Another less widely known use has been in a mixture with oxygen to give a synthetic atmosphere for the use of deep-sea divers and tunnel workers. The advantage is that helium is much less soluble in the body fluids than is nitrogen which is present in air; this substitution prevents "bends," to a large extent. Other uses include mixing with argon and neon in display signs, cooling of electrical equipment, preservation of food, and treatment of respiratory diseases.

ACETYLENE

Acetylene is produced by the reaction of calcium carbide with water.

$$CaC_2 + 2H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2; \qquad \Delta H = -30{,}000 \text{ cal.}$$

The calcium carbide is obtained by heating coke and lime together in an electric furnace as described in Chap. XVII. In plants where a large supply of acetylene is required, generators that automatically feed calcium carbide and water in the correct amounts are used to give a steady supply. Acetylene may also be purchased in steel cylinders which contain disks of felt or porous cement wet with acetone containing the acetylene in solution. This procedure is necessary as acetylene gas, particularly when compressed, decomposes with explosive violence into carbon and hydrogen.

The most important use of acetylene is in the oxyacetylene torches used for welding and cutting metals. Many synthetic organic chemicals, such as acetic acid and synthetic rubber (neoprene), are made from acetylene as a raw material; many more would be synthesized if the price of acetylene could be reduced. Acetylene at one time was much used for illumination, and it still maintains this position in lighthouses or buoys where a light of extreme brilliancy is required.

SULFUR DIOXIDE

Sulfur dioxide may be produced by the burning of sulfur or by the roasting of metal sulfides in special equipment as described in Chap. XIX. It may be obtained also by the recovery from the waste gases of other reactions. The making of sulfur dioxide by the burning of sulfur is the more general method. Its production and the subsequent compression and cooling to form liquid SO_2, which boils at −10°C., are shown in

Fig. 5. With very careful control of the amount of air entering the combustion chamber, sulfur dioxide can be produced up to 18 per cent at a temperature of 1200°C. As the gases from the combustion chamber pass through the heat exchanger, they heat the water for the boilers. The cooled gases, containing from 16 to 18 per cent SO_2, are pumped into the absorbers through acidproof pumps. The strength of the solution from the absorbers is dependent upon the temperature and the strength of the gases entered, but the concentration usually runs from 1.3 to 2 per cent with the temperature close to 30°C. A very small amount of the SO_2 is lost in the exhaust from the second absorber—about 0.02 per cent. The temperature of the vapors coming from the steaming tower depends upon its design but usually runs about 70°C. The vapors are cooled and passed through a drying tower in which 98 per cent sulfuric acid is used. Other drying agents may be employed and some plants by special procedure eliminate the use of this sulfuric acid drier altogether. The SO_2 is liquefied by compressing to about 7 atm. and cooling. It is stored or put into cylinders.

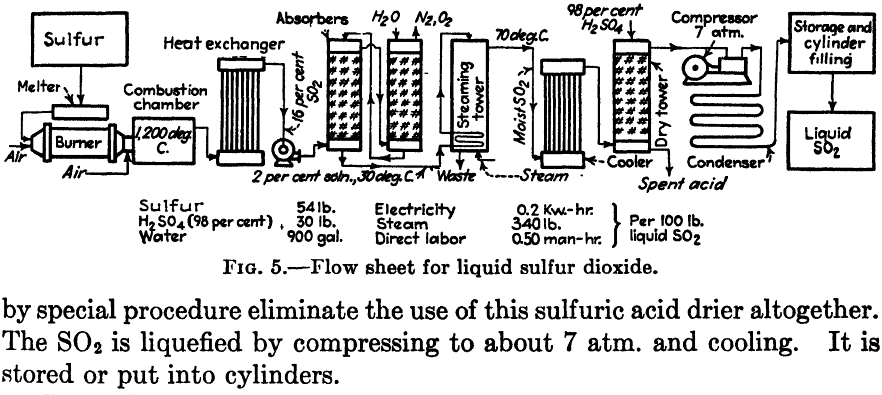

FIG. 5.—Flow sheet for liquid sulfur dioxide.

Sulfur dioxide is shipped as a liquid under 2 or 3 atm. pressure. It is obtainable in steel cylinders[1] of from 50 to 100 lb. capacity, in 1-ton tanks, or in 15-ton tank cars. Its uses are numerous. A quite pure commercial grade containing not more than 0.05 per cent of moisture is suitable for most of its applications. However, a very pure grade, containing less than 50 p.p.m. of moisture is supplied for refrigeration. Sulfur dioxide also serves as the raw material for the production of sulfuric acid. It finds application as a bleaching agent in the textile and food industries. Following the use of chlorine in waterworks or in textile mills, sulfur dioxide is an effective antichlor for removing excess chlorine. It is an effective disinfectant and is employed as such for wooden kegs and barrels and brewery apparatus, and for the prevention of mold in the drying of fruits. Sulfur dioxide effectively controls fermentation in the making of wine. It is used in the sulfite process for paper pulp, as a liquid solvent in petroleum refining, and as a raw material in many plants, for instance in place of purchased sulfites, bisulfites, or hydrosulfites. The convenience of the application of liquid SO_2 has persuaded many small or intermittent users to purchase this rather than to make their own.

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[1] WILLSON, WALKER, RINELLE, and MARS, Liquid Sulfur Dioxide, *Chem. Industries*, **52**, 178 (1943).

CARBON MONOXIDE

Carbon monoxide is one of the chief constituents of water gas as described in Chap. VII. It is obtained in fairly pure form when hydrogen is prepared from water gas by liquefaction of other components, but it is generally used for a fuel in connection with the process. It is an important raw material for methanol (see page 920) and other alcohols and for hydrocarbons.[1] It is a powerful poison.

NITROUS OXIDE

Nitrous oxide is generally prepared by heating very pure ammonium nitrate to 200°C. in retorts.

$$NH_4NO_3 \rightarrow N_2O + 2H_2O(g); \qquad \Delta H = -8{,}800 \text{ cal.}$$

The purification consists in treatment with caustic to remove nitric acid and with dichromate to remove nitric oxide. It is shipped in steel cylinders as a liquid at a pressure of 100 atm. It is used as an anesthetic.

Problems

1. Hydrogen by the steam-iron process is being produced at the rate of 3,500 cu. ft. per hr. If 2.5 times the necessary steam is used, what is the weight of steam used per day?

2. It is desired to market O_2 in small cylinders having volumes of 0.8 cu. ft., each containing 1.5 lb. of oxygen. If the cylinders are subjected to a maximum temperature of 110°F., calculate the pressure for which they must be designed. Assume the applicability of the simple gas law.

3. Calculate the number of hours of service that can be derived from 5 lb. of carbide in an acetylene lamp burning 5 cu. ft. of gas per hour at a temperature of 70°F. and a pressure of 755 mm. of Hg.

4. Calculate the molecular heat of combustion of acetylene from the following data (basis C as *graphite*):

$$\begin{array}{rl}
2H_2 + O_2 \rightarrow 2H_2O; & \Delta H = -2(68{,}375) \text{ cal.} \\
2C + O_2 \rightarrow 2CO; & \Delta H = -2(26{,}390) \text{ cal.} \\
C + O_2 \rightarrow CO_2; & \Delta H = -94{,}030 \text{ cal.} \\
2Ca + O_2 \rightarrow 2CaO; & \Delta H = -2(151{,}700) \text{ cal.} \\
Ca, O_2, H_2 \rightarrow Ca(OH)_2; & \Delta H = -236{,}000 \text{ cal.} \\
Ca, 2C \rightarrow CaC_2; & \Delta H = -14{,}500 \text{ cal.} \\
2C, H_2 \rightarrow C_2H_2; & \Delta H = +54{,}800 \text{ cal.}
\end{array}$$

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[1] UNDERWOOD, Industrial Synthesis of Hydrocarbons from Hydrogen and Carbon Monoxide, *Ind. Eng. Chem.*, **32**, 449 (1940).

5. *a.* How much coke, air, water, and limestone are necessary for the production of 500,000,000 B.t.u. from acetylene?

b. How much of each is necessary if the CO is to be burned also?

6. CO_2 is being absorbed in alkaline solution and heated to recover the pure CO_2. The average CO_2 content in the flue gases entering the absorbing towers is 18 per cent and the gases leaving the towers contain 10 per cent. Of the recovered CO_2 12 per cent is lost in various ways and 88 per cent is recovered as the pure CO_2 product. Calculate

a. The percentage of the entering CO_2 absorbed in the towers.

b. The percentage of the original CO_2 recovered as a final product.

7. By passing a clean purified flue gas up an absorption tower fed with a so-called *lye* solution, made up originally with Na_2CO_3, the CO_2 content of the gas is reduced from 17.1 to 12.1 per cent. The lye solution at entrance and exit is analyzed with 0.2303N HCl, using in each case 10-cc. samples of lye. For the incoming lye 28.21 cc. of acid are required to decolorize phenol-phthalein and a total of 72.30 cc. to get an end point with methyl orange. For the exit liquor these values are 18.41 and 73.16 cc., respectively. 185 gal. of lye per hour are supplied to the tower, which operates at a substantially constant temperature of 150°F.

a. What percentage of the alkali in the two solutions is in the form of bicarbonate?

b. How many pounds of CO_2 are absorbed per hour?

c. What is the volume in cubic feet per hour of the gas entering the tower?

8. By treating dolomitic limestone with sulfuric acid, pure CO_2 can be prepared. The limestone used in such a process contained $CaCO_3$ and $MgCO_3$, the remainder being inert, insoluble materials. The acid used contained 10 per cent H_2SO_4 by weight. The residue from the process had the following composition:

	Per Cent
Water	85.00
$CaSO_4$	8.30
$MgSO_4$	5.00
H_2SO_4	1.00
Inerts	0.60
CO_2	0.10

During the process the mass was warmed and CO_2 and water vapor removed.

a. Calculate the analysis of the limestone used.

b. Calculate the percentage of excess acid used.

c. Calculate the weight and analysis of the material removed from the reaction mass per 100 lb. of limestone treated.

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CHAPTER IX

INDUSTRIAL CARBON

The element carbon exists in three allotropic modifications; these three varieties, namely, amorphous carbon, graphite, and diamond, are also employed industrially.[1] In general, carbon is chemically inert and is infusible at atmospheric pressure. Graphite and diamond resist oxidation even at fairly high temperatures. Some of the industrial applications depend upon the chemical inertness of carbon. On the other hand, the amorphous carbon can be activated, in which case it has a great capacity for selective adsorption from either the gaseous or the liquid state. For nonmetallic substances, carbon and graphite possess a very satisfactory electrical and heat conductivity. The heat conductivity of graphitized, coke-base carbon is superior to that of most metals. Both fabricated amorphous and graphitic carbon products have very low coefficients of thermal expansion and good thermal conductivity, thus giving them high resistance to thermal shock.

Carbon is an extremely versatile element in the way it is of service to man. Its applications are growing each year. Over 15 years ago Mantell[2] wrote, "The possibility of the expansion of the carbon industries is very great, for they are intimately bound up with our highly complex life of the present day." That expansion is now being realized. The helpfulness of carbon is apparent only when we single out the many phases of our everyday living where this adaptable element is essential—in the black pigment of the ink of our books, magazines, and newspapers, in carbon paper, in pencils, as the black color in many paints, automobile finishes, and shoe blacking, as a strengthening and toughening constituent of rubber tires, tubes, and other rubber goods, and as an essential element in the construction of a very large amount of electrical equipment from the household vacuum cleaner to the largest dynamos. The carbon arc is used in the production of visible and ultraviolet radiations for use in an increasingly large number of industrial processes dependent on photochemical reactions. The irradiation of milk to produce a higher vitamin D potency is one example of this use. Carbon and graphite products as structural materials are finding new and increasingly exten-

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[1] The fuel value of carbon as coal is considered in Chap. V.

[2] MANTELL, "Industrial Carbon," D. Van Nostrand Company, Inc., New York, 1928.

TABLE 1.—SOME PROPERTIES OF DIFFERENT MODIFICATIONS OF CARBON[a]

	Amorphous forms			Graphite (artificial)	Diamond
	Coke base	Lampblack base	Anthracite base		
Vaporization temperature	All forms 3925–3970°K.				
Specific gravity	1.98–2.10[b]	1.80–1.85[b]	1.79[b]	2.20–2.24	3.51
Electrical resistivity at 20°C., ohms per cm. cube	0.0035–0.0046	0.0058–0.0081	0.0033–0.0066	0.0008–0.0013	
Specific heat,					
26–76°C.	0.168	....	....	0.165	0.160
26–282°C.	0.200	....	....	0.195	0.315
26–538°C.	0.199	....	....	0.234	0.415
36–902°C.	0.315	....	....	0.324	
47–1193°C.	0.352	....	....	0.350	
56–1450°C.	0.387	....	....	0.390	
Thermal conductivity					
gm.-cal./(sec.)(cm.^{2})(°C./cm.)	0.0125–0.0165	....	0.021–0.025	0.29–0.39	
B.t.u./(hr.)(sq.ft.)(°F./ft.)(or *k*)	3–4	....	5–6	70–94	
Coefficient of thermal expansion per °C. × 10^6 (0–100°C.)	2.41–3.85	....	2.23–2.41	0.97–2.23	

[a] Courtesy of W. C. Kalb, National Carbon Co.

[b] Dependent on source, character of bond, and degree of calcination. The above figures are the real densities of the solids; however, when formed into electrodes where some voids occur, the apparent specific gravity lies in the range of 1.50 to 1.60 for amorphous carbon from coke and in the range of 1.50 to 1.65 for graphite.

sive applications to chemical and metallurgical industries. Electrodes made of carbon and graphite are very important industrial equipment; indeed, electrodes represent the largest single outlet for a carbon product.

Nonfabricated industrial carbon is represented by lampblack, carbon black, activated carbon, graphite, and industrial diamonds. The first three are examples of *amorphous carbon*. *Lampblack* is soot formed by the incomplete burning of carbonaceous solids or liquids. It is gradually being replaced in some uses by *carbon black*, the most important of these amorphous forms and also the product of an incomplete combustion but, in this instance, of natural gas. *Activated carbon* is amorphous carbon that has been treated with steam and heat until it has a very great affinity for adsorbing many materials. *Graphite* is a soft crystalline modification of carbon that differs greatly in properties from amorphous carbon and from the diamond. *Industrial diamonds* are often spoken of as off-grade gems, borts, or carbonadoes and are used for drill points, special tools, glass cutters, wire-drawing dies, diamond saws, and many other applications where this hardest of all substances is essential.

LAMPBLACK

Lampblack or soot is an old product, made for many years by the restricted combustion of resins, oils, or other hydrocarbons. It has been replaced gradually in the pigment trade, particularly in America, by carbon black, which has superior tinting strength and coloring qualities, but in the manufacture of carbon brushes for electrical equipment and lighting carbons, lampblack is still a very important constituent. Its color is a black of a bluish-gray tone, rather than the deep black of carbon black; this steely black is desired for some metal polishes and pencils. Over 5,000,000 lb. are still being produced yearly.

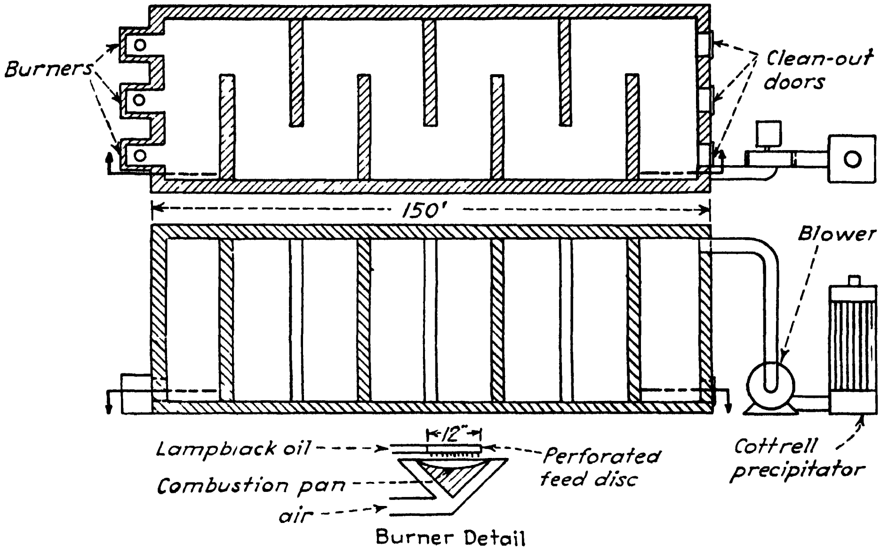

FIG. 1.—Diagram of lampblack house.

In America either tar oils or petroleum oils are burned with restricted air to form soot or lampblack, a suitable furnace being represented in Fig. 1. The soot is collected in large chambers from which the *raw* lampblack is removed, mixed with tar, molded into bricks or *pugs*, and calcined up to about 1000°C. to destroy bulkiness. The calcined pugs are ground to a fine powder. Some furnaces remove the empyreumatic impurities by calcination in the gas stream of the furnaces where formed.

Carbon brushes for use in electrical machinery are made by mixing lampblack with pitch to form a plastic mass. Petroleum coke or graphite may be added to this mix to impart special properties. Plates or blocks from which the brushes are later machined are formed by extrusion or high-pressure molding, and these *green* plates are then baked at a high temperature for several days to drive off volatile matter. Some grades are heated in electrical furnaces at temperatures as high as 3000°C. (5432°F.) to convert the amorphous carbon into the soft, crystalline graphite which reduces the friction, increases the life, and generally improves the quality of the product (*cf.* Graphite, page 157).

When carbons for the production of special arc lights are desired, a mixture of petroleum coke and Thermatomic carbon is extruded in the form of a tube. This tube is baked at 1450°C. and a *core* of selected material is forced into its center and calcined again. The type of radiation emitted by the arc is largely dependent on the core material employed, which is frequently a mixture of some lampblack flour, rare-earth oxides, and fluorides with coal tar as a binder. Over 6,000,000 such lighting carbons are sold per month in peace times for movie projectors. In war years, a great quantity of such lighting carbons are consumed by searchlights.

CARBON BLACK

The first factory for the making of carbon black[1] in this country was built at New Cumberland, W. Va., in 1872. The black was produced by burning a gas flame against soapstone slabs and scraping off the carbon produced. A short time later, 1883, the roller process was patented and, in 1892, McNutt perfected the present-day channel process. Early production was moderate, 25,000,000 lb. per year, West Virginia and Pennsylvania being the only two producing states.

In the summer of 1912, however, the B. F. Goodrich Company, having been convinced of the value of carbon black in the rubber industry, ordered a carload of the material, and later in the same year placed an order for 1,000,000 lb. per year. The advent of this new market stimulated the industry. Expansion has been rapid but, since natural gas is the raw material, the industry has been forced to follow the excess gas supply as it changed from Pennsylvania to Indiana, West Virginia,

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[1] In a sense, carbon black is a variety of lampblack, both being produced by the incomplete burning of hydrocarbons. However, carbon black is the product from natural gas. Both lampblack and carbon black are the same chemically, being over 99 per cent C, but they differ greatly in their physical form such as shape of the particles and also in adsorbed gases.

Louisiana, and more recently to Texas,[1] where more than 85 per cent of the present carbon black is produced. The selling price has been constantly reduced in keeping with the expansion of the industry, dropping from $2.50 per lb. in 1872 to as low as 3.4 cents per lb. in 1940.

Uses and Economics.—In 1941, the domestic consumption of carbon black was divided as follows: rubber companies, 83 per cent; ink manufacturers, 5.3 per cent; paint manufacturers, 1.0 per cent; miscellaneous uses, including exports, 10.7 per cent.[2]

There are three different grades of carbon black that go into the rubber industry[3]: slow curing, medium curing, and fast curing, so designated because of the degree to which they work with organic accelerators in the rubber mix. The addition of carbon black to the rubber not only colors the product black but also gives the *wear-resistant* properties necessary to tires, rubber heels, and various mechanical goods. Thus, approximately 20 to 40 per cent of carbon black is present in the rubber compound of the modern tire, a major contributing factor in placing this industry at the head of the list of consumers of carbon black.

The second most important consumer is the printing ink industry where carbon black is the basis of most newsprint, job, letter press, book, carton, bag, gravure, and rotary inks. The carbon blacks for this industry must be uncompressed, grind easily, and absorb oil readily. The pigment in black resins, paints, lacquers, and enamels also usually consists of carbon black. The properties required for this demand are low bulk, ease of grinding, jet-black color, good suspension, and low oil adsorption. Other uses for the blacks include coatings for carbon paper or typewriter ribbons and color in phonograph records.[4] Mixed with liquid oxygen it forms an explosive more powerful than dynamite.

In 1941, 594,065,000 lb. of carbon black were produced in the United States. Of this total, over 82 per cent was manufactured by the channel process. It is estimated that about 365,377,000,000 cu. ft. of natural gas were burned to produce this poundage.[5]

Manufacture.—Carbon black is produced solely from natural gas as a raw material.[6] This gas, after suitable treatment to remove the valuable natural gasoline present, consists chiefly of methane with some ethane. Since it is almost a waste product, it is extremely cheap, the current price being around 2 or 4 cents per M cu. ft. This allows the selling of carbon black at a low price in spite of the poor yield from the carbon in the gas. There are four different industrial processes, of which the first is by far the most important: the channel process, the Lewis process, the Gastex process, and the Thermatomic process.

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[1] The plant of the Continental Carbon Co., Sunray, Tex., comprises 366 production buildings covering 160 acres. Here, night and day, 1,185,840 small flames, burning natural gas, play on the moving channels. *Ind. Eng. Chem., News Ed.*, **16**, 114 (1938).

[2] Mineral Industry Surveys, M. M. S. 998, U.S. Department of Interior, Bureau of Mines, 1942.

[3] STILLWAGON, Pioneering Carbon Black in American Tires, *India Rubber World*, **96**, No. 4, 39 (1937).

[4] JOHNSON, Carbon Black Manufactured from Gas, *India Rubber World*, **98**, No. 3, 40 (1938).

[5] Mineral Industry Surveys, *op. cit.*

[6] HAYNES, Bead Process Gives Clean Carbon Black, *Chem. & Met. Eng.*, **45**, 187 (1938); GRUSE and STEVENS, "The Chemical Technology of Petroleum," 2d. ed., McGraw-Hill Book Company, Inc., New York, 1942.

Channel Process.—Since approximately 80 per cent of the carbon black produced in the country is made by the channel process, a description of this procedure is presented. The conversion realized in practice is only about 3 per cent of the total carbon.

Unit Operations, Unit Processes, and Energy Changes.—The changes involved in the carbon black channel procedures are

Natural gas is "dried" of its gasoline, usually by absorption (Op.).

Natural gas is cracked or pyrolyzed against a moving and cooled channel iron (Pr.); here the temperature of the products of combustion of 1000 to 1200°C. is reduced to 500°C.

Carbon black is scraped off the channel, conveyed to packing house, sifted, and packaged (Op.).

Reactions:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(g); \qquad \Delta H = -191{,}800 \text{ cal.} \qquad (1)$$

$$CH_4 \rightarrow C \text{ (amorph.)} + 2H_2; \qquad \Delta H = +20{,}300 \text{ cal.} \qquad (2)$$

In manufacturing carbon black the very low chemical efficiency of changing CH_4 to C, whereby the unconverted CH_4 and the H_2 burn completely to CO_2(CO) and H_2O, supplies the heat and energy necessary to crack or pyrolyze CH_4 to C. Thus, no outside energy input is needed here. However, as 1 M cu. ft. of CH_4 contain 31 lb. of C, while the yield is only 1 lb. of carbon black, it is seen that there is great wastage.

The natural gas, as it comes from the ground, is first treated to remove the natural gasoline and then sent to the burner houses. These are long, low sheet-iron buildings containing from 3,000 to 4,000 burner tips where the gas is burned with an insufficient supply of air, controlled by the sides of the sheds, to produce a luminous flame that impinges on the underside of the channels. The channels, made of mild steel and 6 to 8 in. wide, move continuously backward and forward suspended from overhead rails. The carbon black thus produced is removed from the channels as they pass over stationary scrapers and falls into hoppers which feed screw conveyers carrying the carbon to the central packing house. The spent gases escape to the air. They contain considerable quantities of black, as evidenced by the dark pall that always overhangs the plant, but it has never proved economical to install a system for the recovery of this waste. In the packing house the black is *bolted.* This is merely a separation to remove coarse particles and grit. The material is extremely light and fluffy and must be agitated to condense the bulk. The resulting black is a commercial grade known as *uncompressed;* its density is 13 lb. per cu. ft., and it is used in the paper, ink, and paint industries.

For use in the rubber industry, the black must be compacted to reduce the tendency to dust. In this operation it is packed in strong paper sacks that leak a little air and is compressed in hydraulic or mechanical presses. The most popular form on the market is the double-compressed grade in a 6- by 6- by 22-in. package weighing 12.5 lb. A newer process[1] makes dustless pellets from the uncompressed black by running a water paste of the same over a long table containing small rotating pins. The particles gradually assume a rounded contour and are forced into pellets by the constant agitation. These are dried in a 30-ft. rotating steel cylinder at 150°F. and shipped in paper bags or in specially designed tank cars.

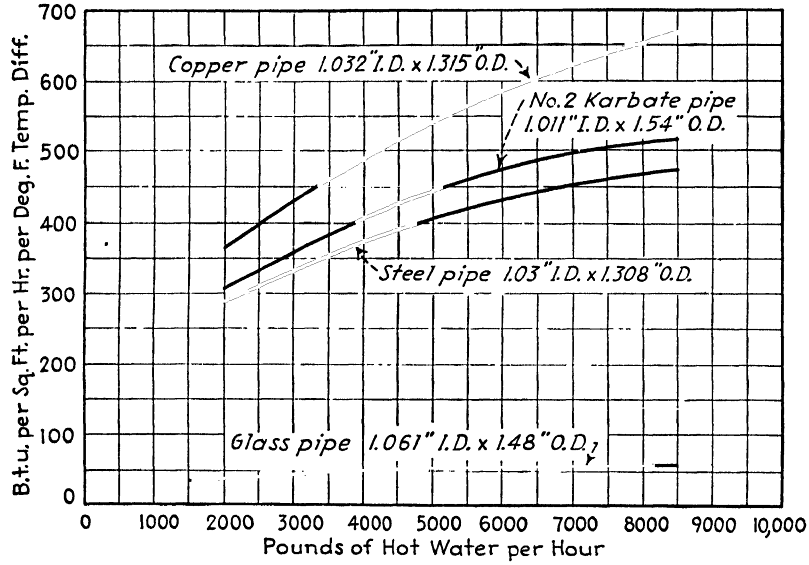

FIG. 2.—Comparative over-all heat transfer. The curves show comparative rates of heat transfer through 1-in. standard copper, steel, glass, and No. 2 Karbate pipes. The test was hot water to cold water with the cold water held at 12,000 lb. per hr. throughout the test. (*Courtesy of National Carbon Company.*)

Other Processes.—Carbon black is also manufactured by the disk and roller processes. The former is very similar to the channel process, the flame merely impinging on a moving disk instead of a channel. The latter produces a special type of black which is used in the ink industry.

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[1] HAYNES, *op. cit.*

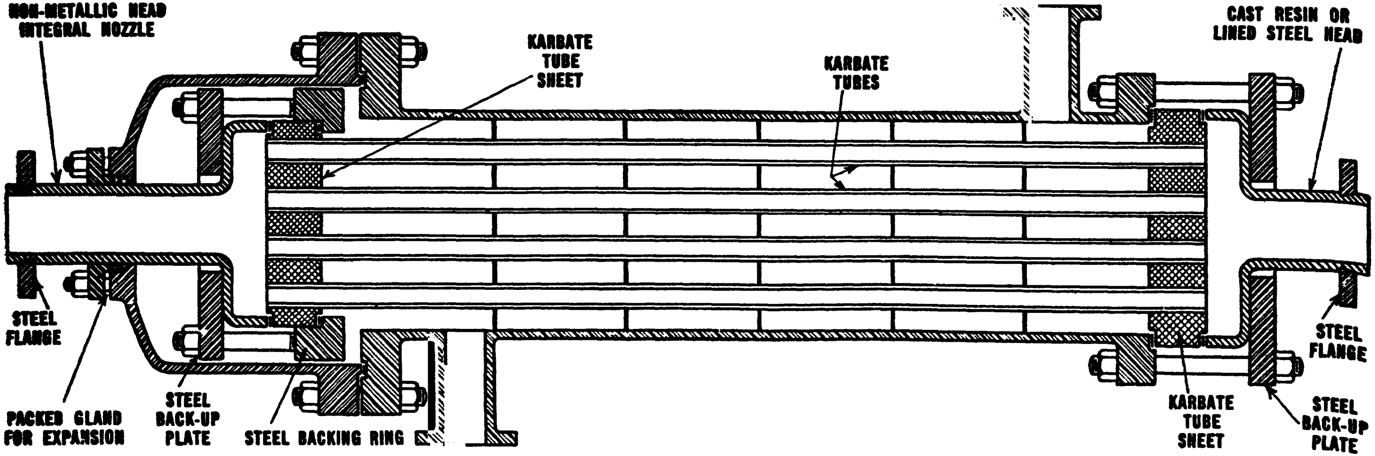

FIG. 3.—Sectional view—graphite tube exchanger—single tube pass: used for heating dilute sulfuric acid in rayon processing. (*Courtesy of Struthers-Wells.*)

The other processes for producing *blacks* (Lewis, Gastex, and Thermatomic) employ specially designed furnaces burning natural gas and producing soft blacks for rubber compounding. For the Lewis process, the gas is burned in a regulated amount of air, producing flames about 6 ft. in diameter.[1] The black appears as dense clouds of smoke. These are condensed in water, settled, filtered, dried, and powdered. Also, in the Gastex process the gas is burned in a limited supply of air. The product, however, is collected by electrical precipitation. The Thermatomic process might be described as a cracking process in which natural gas is split into hydrogen and carbon by passage over heated brick checkerwork above 1600°F. The reaction is

$$CH_4 \rightarrow C\ (\text{amorph.}) + 2H_2; \qquad \Delta H = +20{,}300\ \text{cal.}$$

In practice the gas is passed downward over the heated brick, the hydrogen and about half of the carbon being removed at the bottom of the furnace, cooled by a water spray, and the black being collected with a yield of 6 to 10 lb. of carbon from 1 M cu. ft. of natural gas. The remainder of the carbon remains on the brickwork. After a short period, the natural gas stream is shut off and heating gas and air passed through the checkerwork from the opposite direction. This ignites the coating of carbon which burns, thereby aiding in reheating the furnace for a new cycle.

CARBON AND GRAPHITE STRUCTURAL MATERIALS

Largely because of chemical inertness, the use of carbon and graphite in various structural shapes has been increasing. Bricks in different forms were early made by binding together the carbon with a suitable pitch, pressing into shape, and baking. By supplementing the pitch binder with a chemical-resistant resin, such as one derived from phenol-formaldehyde, the porosity of the ordinary pitch-bound brick is reduced, and the strength and chemical resistance increased. This has enabled pipes, valves, fittings, Raschig rings, and a great many other shapes to be economically constructed, so that this use of carbon[2] has become practical.

As Table 1 shows, carbon has very desirable physical and chemical properties. It is resistant, even in the cemented variety, to a great many of the usual acids both organic and inorganic. Thus, these structural shapes have been extensively employed in plants handling hydrochloric acid, phosphoric acid, hydrofluoric acid, citric acid, and many other corrosive chemicals, at temperatures up to 170°C. Although carbon in these forms is first attacked by certain chemicals such as 20 per cent ammonium hydroxide, 50 per cent zinc chloride, and gasoline, it is fairly resistant after this initial attack and can be practically used. Although this structural carbon is seriously attacked by the strongly oxidizing chemicals such as wet chlorine, 5 per cent hypochlorite, and even 1 per cent nitric acid, it often proves more durable than any other material available.

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[1] Drogin, Carbon Black for the Process Industries, *Chem. & Met. Eng.*, **43**, 139 (1936).

[2] National Carbon Company, Inc., has put such products on the market under the trademark Karbate. Karbate No. 10 series is a petroleum coke base carbon material made impervious by impregnation with a suitable resin. Karbate No. 20 series is the same base material which has been graphitized in an electric furnace prior to impregnation.

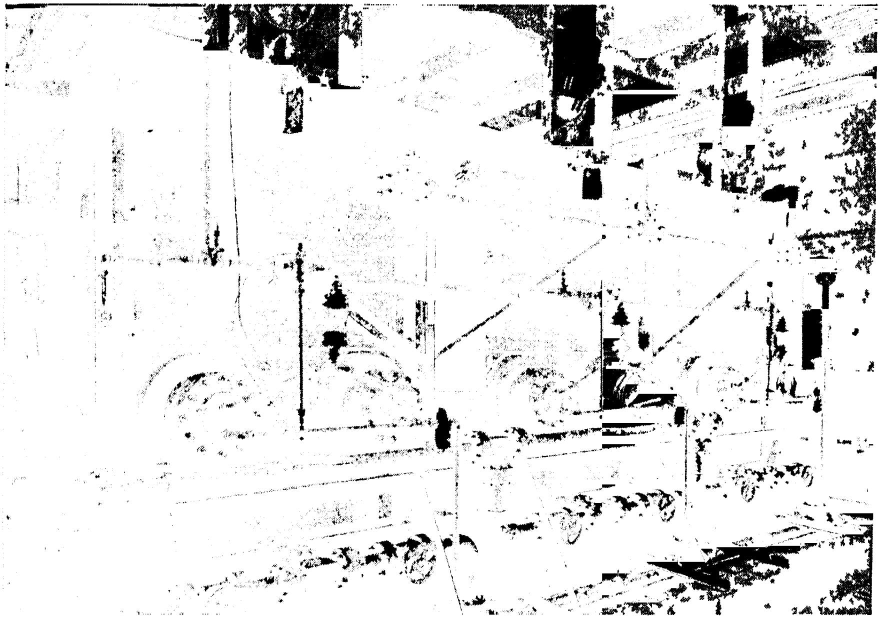

FIG 4 —Front view of ore leaching tanks The tanks are fabricated completely from 2-in thick slabs of Karbate No 28 cemented together at all joints with special cement. Note Karbate pipe and fittings Neoprene sleeves are provided for expansion of metal pipe supports (*Courtesy of National Carbon Company*)

Graphite has high thermal conductivity with a low coefficient of thermal expansion, which makes it suitable for pipes and fittings, heat exchangers, and heating coils, using steam up to 50 to 75 lb. pressure. Figures 2 to 5 give examples of this interesting application of industrial carbon; Fig. 2 depicts comparative heat-transfer coefficients; and Figs. 3 to 5 illustrate technical installations. A recent important extension of structural carbon is for complete fabrication of all parts (except lead drip pans and lead-coated electrical conductors) of Cottrell precipitation towers for sulfuric acid. The carbon can be easily fabricated into porous plates, pipes, and devices for diffusing gases into liquids, or for filtering solids from acids, water, or other liquids, or for aeration of liquids. Carbon beams are now available in sizes up to 2 by 2½ by 15 ft.

Carbon structural forms are made very much the same as carbon electrodes, except that this material, as it comes from the final calcining furnace, is too porous to hold liquids and therefore must be impregnated to make it relatively impervious. This is done frequently with a phenol-formaldehyde or phenol-furfural resin. The process of changing an amorphous carbon to graphite is described under Graphite (page 157). This change increases the heat and electrical conductivities and also enables more intricate machining to be used in fabricating complicated parts.

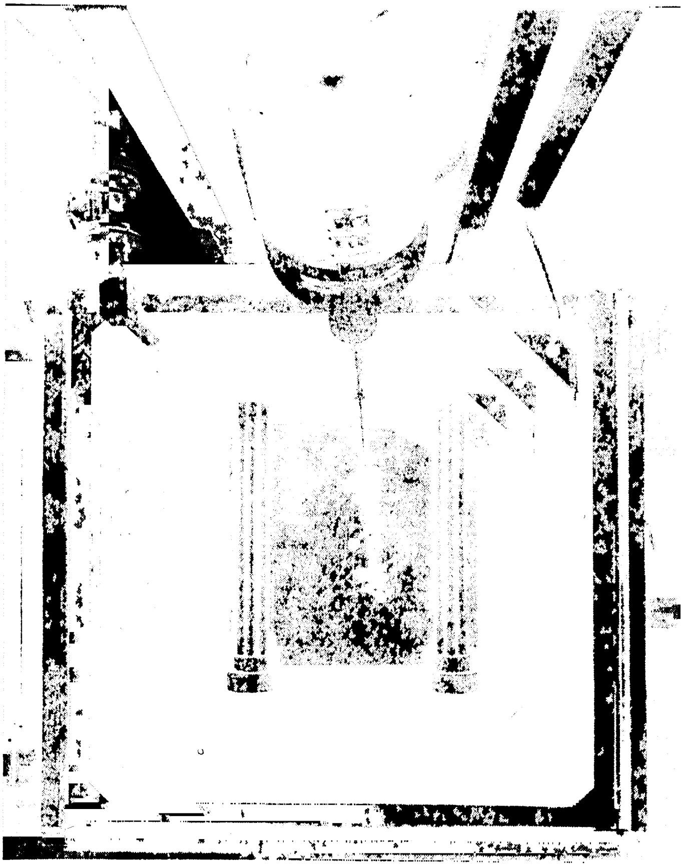

FIG. 5.—Top view of ore leaching tanks Karbate No 28 bundle-type heaters are shown in place. These bundles are removable (*Courtesy of National Carbon Company*)

ACTIVATED CARBON

The product known as activated carbon is a material that first came into prominence through its use as an adsorbent in gas masks in the First World War. However, the knowledge that carbon produced by the decomposition of wood can remove coloring matter from solutions dates back to the fifteenth century. The first commercial application of this property was not made, however, until 1794, when charcoal filters were used in a British sugar refinery. About 1812, bone char was discovered by Figuer. At the present time, however, activated carbon[1] is the material being employed for most carbon decoloration problems and is even gradually replacing bone black in the sugar industry. Another type of activated carbon has the ability to adsorb gases and vapors.

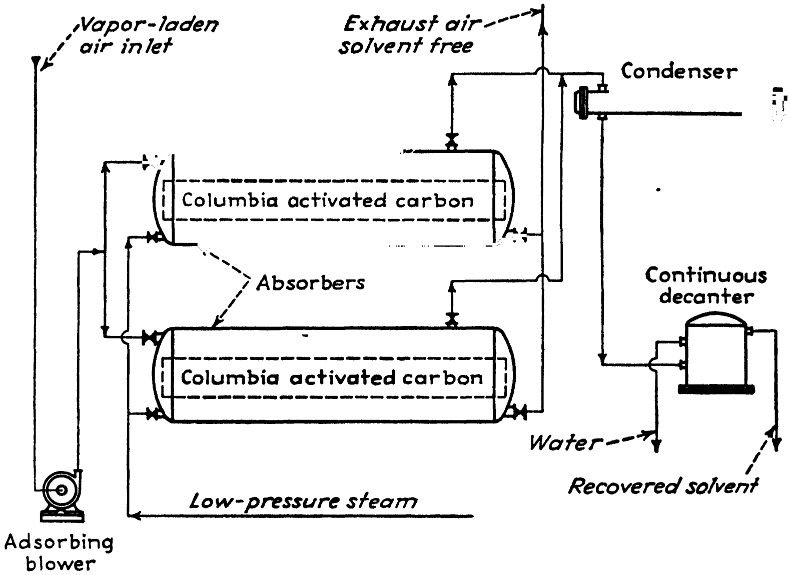

Fig. 6.—Flow diagram of one type of solvent recovery plant employing Columbia activated carbon. A typical plant of this type in recovering a hydrocarbon vapor at a rate of 1,100 lb. per hr. from 13,000 cu. ft. per min. of vapor-laden air will have the following approximate average utility requirements per pound of recovered solvent: Steam—3.5 lb.; water—7.5 gal.; electric power—0.05 kw.-hr. *(Courtesy of Carbide and Carbon Chemical Corporation.)*

Uses.—Activated carbon is hundreds of times more efficient as a decolorant than charcoal and at least forty times more effective than bone black. This increased activity is due entirely to the very great surface area of the material. It is estimated that 5 lb. of activated carbon has an active surface area of 1 sq. mile or more. Adsorption is a physical phenomenon depending largely upon the surface area.[1]

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[1] Hassler, "Active Carbon—The Modern Purifier," bibliography, Githens-Sohl Corporation, New York, 1941.

There is no particular activated carbon that is effective for all purposes, one type being suited as a decolorant and purifying agent for liquids, another as a vapor adsorbent. The vapor-adsorbent type was first used in military gas masks because of its ability to adsorb certain poisonous gases and is now widely employed in both military and industrial gas masks. Another field of application is in the industrial recovery of vapors (see Fig. 6), such as natural gasoline from natural gas or alcohol from carbon dioxide from fermenters. The development of the hydrogenation of oils has led to a new use of the decolorizing type of activated carbon as a decolorant and deodorant in the oils and fats industry. It has replaced fuller's earth to some extent in the petroleum industry and is replacing bone black in the sugar industry. The amount of other material adsorbed by activated carbon is surprisingly large,[2] amounting frequently to from a quarter to an equal weight of such vapors as gasoline, benzene, or carbon tetrachloride. These substances can be *recovered and reused.* Some of the many uses of both types of activated carbon are presented in Table 2.[3]

Manufacture.—Many carbonaceous materials, such as sawdust, lignite, coal, peat, wood, charcoal, nutshells, and fruit pits, may be used for the manufacture of activated carbon, but the properties of the finished material are naturally governed by the source.[4]

Decolorizing activated carbons are usually employed as powders. Thus the raw materials for this type are either structureless or have a weak structure. Sawdust and lignite yield carbons of this kind. Vapor-adsorbent carbons are used in the form of hard granules and are generally produced from coconut shells, fruit pits, and briquetted coal and charcoal.

Activation is a physical change wherein the surface of the carbon is tremendously increased by the removal of hydrocarbons from the carbon surface. Several methods are available for the activation of charcoal. The most widely employed are the treatment of the carbonaceous material with oxidizing gases such as air, steam, or carbon dioxide, and the carbonization of the raw material in the presence of chemical agents such as zinc chloride or phosphoric acid.

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[1] For an excellent discussion of the theories of adsorption see Lewis, Squires, and Broughton, "Industrial Chemistry of Colloidal and Amorphous Materials," Chap. 5, The Macmillan Company, New York, 1942.

[2] PERRY, *op. cit.*, p. 1317.

[3] Mantell's section on Adsorption in Perry, *op. cit.*, should be consulted for formulas pertaining to adsorption, flow sheets of plants using adsorbents, engineering data, and generalized theory of adsorption, particularly pp. 1270, 1277, 1294–1322; on p. 1312 is given a tabular comparison of activated carbon, activated alumina, and silica gel. *Cf.* STRACHEM, Some Industrial Applications of Activated Carbons, *Chemistry & Industry*, **47**, 1203 (1928); LEWIS, SQUIRES, and BROUGHTON, *op. cit.*

[4] WILLIAMS, Activated Carbon from Coal, *Engineer*, **159**, 203 (1935).

The gaseous oxidation activation employs material that has been carbonized at a temperature high enough to remove most of the volatile constituents but not high enough to crack the evolved gases. The carbonized material is subjected to the action of the oxidizing gas, usually steam[1] or carbon dioxide, in a furnace or retort at 800 to 1000°C. Conditions are controlled to permit removal of substantially all the adsorbed hydrocarbons and some of the carbon so as to increase the surface area.

FIG 7.—View of solvent recovery plant using Columbia activated carbon. Absorbers are in the open while other equipment is housed. Equipment arranged for addition of other adsorbers when increased capacity is required. (*Courtesy of Carbide and Carbon Chemical Corporation*)

The use of chemical impregnating agents causes the carbonization to proceed under conditions that prevent the deposition of hydrocarbons on the carbon surface. The raw material, sawdust or peat, is mixed with the chemical agent, dried, and calcined at temperatures up to 850°C. When the carbonization has been completed, the residual impregnating agent is removed by leaching with water.

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[1] CHANEY, U.S. Pat., 1499908 (1924).

Revivification.—After an activated carbon has become saturated with a vapor or an adsorbed color, either the vapor can be steamed out, condensed, and recovered as shown in Fig. 6, or the coloration can be destroyed and the carbon made ready for reuse. The oldest example of this process is exemplified by that decolorizing carbon long known as *bone char* or *bone black.*[1] This consists of carbon deposited on a skeleton of tricalcium phosphate and is made by the carbonization in closed retorts at 750 to 950°C. of fat-freed bones. Over 50,000,000 lb. of bone char with a value of around $2,500,000 to $3,000,000 are produced annually in the United States, and much of this is employed in the manufacture of sugar.[2] After saturation with impurities, the bone char is washed free from sugar and recalcined at around 750°F. under

TABLE 2.—APPLICATIONS OF ACTIVATED CARBON[a]

A. Adsorbing Gases or Vapors (Gas-adsorbent Carbon):
  1. Adsorbent in military and industrial gas masks and other devices.
  2. Recovery of gasoline from natural gas.
  3. Recovery of benzol from manufactured gas.
  4. Recovery of solvents vaporized in industrial processes such as manufacture of rayon, rubber products, artificial leather, transparent wrappings, film, smokeless powder, and plastics, and in rotogravure printing, dry cleaning of fabrics, degreasing of metals, solvent extraction, fermentation, etc.
  5. Removing impurities from gases such as hydrogen, nitrogen, helium, acetylene, ammonia, carbon dioxide, or carbon monoxide.
  6. Removing organic sulfur compounds and other impurities from manufactured gas.
  7. Removing odors from air in air conditioning, stench abatement, etc.

B. Decolorizing and Purifying Liquids (Decolorizing Carbon):
  1. Refining of cane sugar, beet sugar, glucose, and other sirups.
  2. Refining oils, fats, and waxes such as cottonseed oil, coconut oil, lard, and mineral oil.
  3. Removing impurities from food products such as gelatine, vinegar, cocoa butter, pectin, fruit juices, and alcoholic beverages.
  4. Removing impurities from pharmaceutical and other chemical products, including acids.
  5. Water purification—removal of taste, odor, and color.
  6. Removing impurities from used oils, dry-cleaning solvents, electroplating solution, sirups, etc.
  7. Removal of metals from solution—silver, gold, etc.

C. Catalyst and Catalyst Carrier (Gas-adsorbent Carbon):
  1. Manufacture of phosgene.
  2. Carrier for hydrogenation catalysts, etc.

D. Medicine:
  1. Internal medicine for adsorption of gases, toxins, and poisons.
  2. Administering adsorbed medicinals.
  3. External adsorbent for odors from ulcers and wounds.

[a] RAY, Carbide and Carbon Chemicals Corp.

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[1] PERRY, *op. cit.*, pp. 1294–1298, including flow charts.

[2] See Chap. XXX.

restricted oxidizing conditions that destroy the impurities and restore the adsorbing properties of the carbon.

GRAPHITE

Graphite, as it occurs naturally, has been known to man for many centuries. Probably its first use was for decorative purposes in prehistoric times. By the Middle Ages it was being employed for writing and drawing purposes, mention of this being found in the literature of those times. The name *graphite* was given to this substance by the mineralogist Werner, in 1879. Natural graphite was the only kind available except in laboratory quantities until 1896, when Edward G. Acheson invented the first successful process for the commercial production of artificial graphite, as an outgrowth of his work on silicon carbide. He discovered that, when most forms of amorphous carbon are placed together with certain catalysts such as silica or alumina in an electric furnace and subjected to a temperature of approximately 3000°C., they are converted into the allotrope, graphite. Since that time many improvements have been made on Acheson's process. It is now known that amorphous carbon can be converted directly to graphite in an electric furnace, by a process that is practiced industrially.

Uses and Economics.—About 10 per cent of the United States consumption of *natural graphite* goes into the manufacture of crucibles. For this purpose it is mixed with clay, sand, and water and then set away to age. The crucible is formed on "jiggers" and then air-dried and baked in a kiln. The graphite of the crucible wall begins to oxidize at about 450°C., and the life of the crucible depends on keeping the *rate* of oxidation down. This rate depends on temperature but also on composition of furnace gases and of binder or glaze. Bricks and various other graphite products are also produced. Another large consumer of natural graphite is the pencil industry, which requires a fairly pure raw material containing around 90 per cent graphite. Natural graphite is also employed in metallic graphite brushes for electrical machinery. The lower grades of the natural material, containing 35 to 50 per cent carbon, are used[1] in paints, stove polishes, lubricants, etc.

The United States production of *natural graphite* has been practically nonexistent or small in recent years. Imports, however, have continued at around 17,000 tons (1938), over two-thirds of which came from Mexico in some years. Natural graphite, frequently called *plumbago*, is mined in many sections of the world, particularly in Ceylon, Madagascar, Bavaria, Chosen, Russia, Canada, and Mexico. No figures on the United States production of artificial graphite are available. Total world production of all graphite in 1938 was 140,569 metric tons, excluding Russia and the United States. In 1928, the United States produced over $12,000,000 worth of carbon and graphite electrodes.

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[1] SZYMANOWITZ, Preparation, Properties and Uses of Colloidal Graphite, *J. Chem. Education*, **16**, 413 (1939).

Artificial graphite can be substituted for any of the uses of the natural product except in the making of clay-graphite crucibles, although many crucibles and trays of artificial graphite are manufactured. On the other hand, the very pure artificial graphite has many fields of exclusive use, such as a high-temperature lubricant or for electrodes in various chemical manufactures. For lubricating purposes it is suspended in water or oil and placed in contact with the moving parts. The liquid media evaporate, leaving the graphite well distributed over the entire surface. The electrical industry uses graphite for electrodes, brushes, contacts, and electronic-tube rectifier elements. A considerable amount is employed for a parting compound to prevent molds of such articles as glass bottles and rubber tires from sticking together. Various friction elements, such as brake linings, are treated with graphite to prevent grabbing, and it is incorporated as an ingredient in lubricating oils and greases.

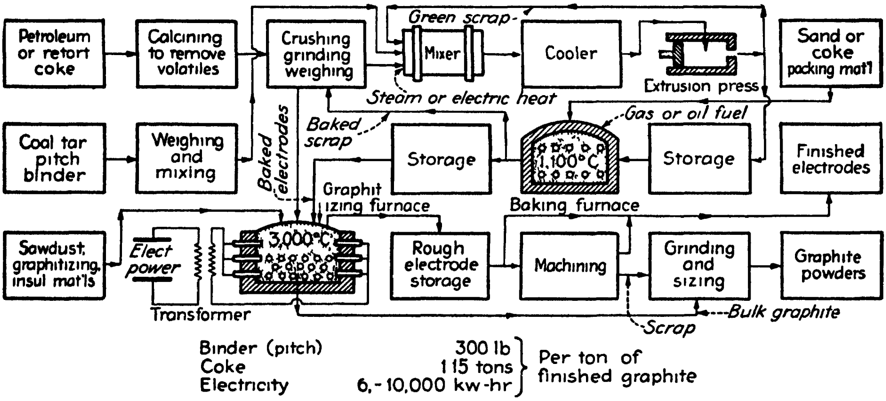

FIG. 8.—Flow sheet for manufacture of artificial graphite electrodes and powders.

Manufacture.—*Artificial graphite* is made electrically from retort or petroleum coke, in line with the flow sheet depicted in Fig. 8. The reaction for this allotropic change is essentially,

$$\text{C (amorph.)} \rightarrow \text{C (graphite)}; \qquad \Delta H = -2{,}500 \text{ cal.}$$

The *unit changes* involved in commercializing these reactions, as charted in Fig. 8, may be summarized for electrodes or other graphite articles:

Coke (petroleum or retort) is selected and shipped to graphite plant (Op.).
Carbon material is calcined (1400°C.) to volatilize impurities (Op. and Pr.).
Raw materials are carefully analyzed.

Raw materials are ground, mixed with binder, giving green electrodes, and arranged in furnace (Op.).

Green electrodes are baked at 1100°C. to carbonize binder and furnish amorphous electrodes (Pr.).

Amorphous electrodes are graphitized in electric furnace at high temperature (3000°C.) (Pr.).

Graphite is shaped to industrial demands and the scrap powdered (Op.).

In manufacturing graphite the furnace used consists essentially of a core of the coke being graphitized, surrounded by a heavy layer of sand, coke, and sawdust as insulation. The floor and ends of the furnace are built mainly of concrete, with cooling coils in the ends to reduce the temperature of the electrodes in contact with air to prevent them from burning. The side walls, built of loose blocks and plates, are torn down after each run. The average charge is approximately 30,000 lb. of material. The resistance of the charge produces a temperature of around 3000°C. As the coke graphitizes,[1] the voltage, owing to lowered resistance, drops from 200 to 40 volts. The high temperature employed decomposes, for instance, any silicon carbide that may be present and

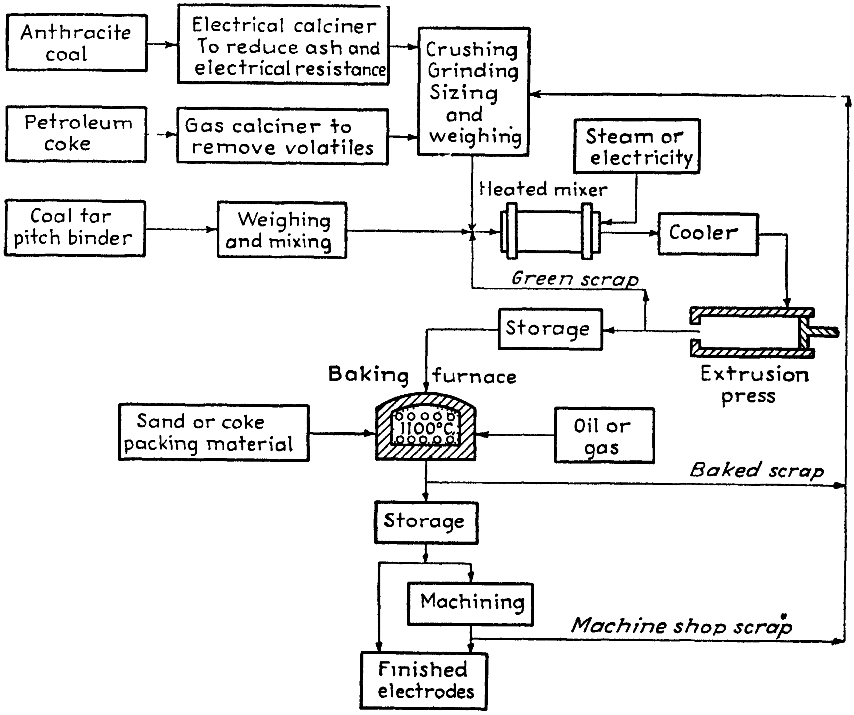

FIG. 9.—Flow chart for manufacture of amorphous carbon electrodes.

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[1] SPRAGUE, The Graphitizing Furnace, *Trans. Electrochem. Soc.*, **70**, 57 (1936).

volatilizes products other than graphite. A complete cycle of the furnace consists in: loading, 1 day; power on, 5 to 6 days; cooling, about 25 days; unloading, 2 days. Thus about 1 month is required from charge to charge. After cooling, the furnace is torn down and the graphitized carbon taken out, crushed, and ground. The insulating sand is used over again.

In the manufacture of *amorphous carbon electrodes*[1] the petroleum coke or anthracite used is crushed and hot mixed with a pitch binder thinned with oil (see Fig. 9). The resulting soft mass is either extruded or molded to the finished electrode shape. These green electrodes are then baked at around 1100°C. in either a gas-fired furnace or an electric furnace. After cooling and removal from the furnace these electrodes are turned down and threaded on a lathe. A similar process is involved in making brushes for motors, the carbon being made into small plates which are then cut to the necessary shape for making the brushes. Graphite electrodes have less electrical resistance and consequently can conduct more current per cross section, but they cost more than the usual amorphous[2] carbon electrode.

INDUSTRIAL DIAMONDS

Because the diamond is the *hardest* and most permanent of all known substances, it has great industrial importance in cutting, shaping, and polishing hard substances. For a thousand years diamonds have been employed for this purpose in the East. Their use is increasing particularly in countries like the United States where much high-speed machining of hard materials is required. Consequently this country is the largest consumer of industrial diamonds in the world. The world consumption of industrial diamonds is estimated[3] to approach 7,500,000 carats (3,300 lb.) for 1942.

Three types are employed: (1) crystalline and cleavable *diamonds* more or less off grade and off color, (2) *bort*, translucent to opaque, gray or dark brown, with a radiated or confused crystalline structure (inferior grade of crystalline diamonds are also called *bort*), (3) *carbonado*, frequently known as a *black diamond* or carbon. It occurs in an opaque, tough, crystalline aggregate without cleavage. It is composed of diamond, graphite, and amorphous carbon. The bort is the most widely used of the industrial diamonds.

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[1] Detailed flow sheets for both graphite and carbon electrodes are given by Mantell on p. 726 of "Rogers' Industrial Chemistry," 6th ed., D. Van Nostrand Company, Inc., New York, 1942.

[2] For a tabular comparison of the properties of graphite and amorphous carbon electrodes, see Perry, *op. cit.*, pp. 2820, 2821–2828.

[3] Ball, Gem Stones, "Minerals Yearbook," 1941, U.S. Bureau of Mines, Washington, D.C., 1942.

The bulk of industrial diamonds comes from Brazil and South Africa. Bort-prepared diamond powder costs about $2 a carat, although bort, if bought as mined and in 50 to 100 lb. quantities, may be priced as low as 60 cents a carat.[1] Carbonado usually sells for a much higher price than bort. In addition to the usual industrial varieties there are available chips and small fragments of gem diamonds which however are utilized in the making of diamond powder for polishing gem diamonds and other hard materials. These chips also serve as the "point" in glass cutters. Altogether about four-fifths of the total diamonds mined throughout the world is available only for industrial application.

TABLE 3.—CHIEF USES FOR INDUSTRIAL DIAMONDS, BY VALUE[a]

	Per Cent
Diamond drilling	45–50
Diamond-set tools	30–35
Diamond dies	10–7
Crushing bort for bonded wheels and tools	10–7
Miscellaneous	5–11

[a] BALL, Gem Stones, "Minerals Yearbook," 1941; U.S. Bureau of Mines, Washington, D.C., 1942.

An extensive use of industrial diamonds is to face lathe tools after the industrial diamonds are appropriately shaped. The *extreme hardness* of the diamond and the fact that *it is not affected by an increase in temperature* during the operation of a lathe enable the operator greatly to increase machining speed. The tougher carbonado is best suited to this service, but the bort is more widely employed because of its relatively low price. Tools set with uncut diamonds are a practical necessity in truing worn abrasive wheels, particularly in our large automobile factories. Bort is also used. Bonded diamond wheels and saws for shaping hard materials, such as cemented carbide tools and the like, are made from crushed bort. Since the continual drawing of wire through dies causes much wear, dies for accurate wire drawings are made out of diamonds. Such dies are preferably made from cleavage sections of bort or diamond crystals, with an appropriate hole drilled therein. Such holes are started by sharp diamond points but finished by a steel drill revolving in diamond dust. Such dies should be carefully mounted so that they will not be fractured while in use. They last about 2 years, when they must be redrilled to the next larger size of wire. In *drilling* through rock for oil or water or for the placing of dynamite in quarries, the steel drill bits are set with the tough uncut carbonado or occasionally bort in metallic heads; here the diamonds do the actual work, the steel heads simply serving to hold them in the cutting position. These diamond drills enable actual cores of the rock to be taken out and examined with consequent greatly increased knowledge of what minerals or deposits lie underground. This most valuable means of exploration was first used in the United States by the St. Joseph Lead Company in 1869 when exploring for lead ores at Bonne Terre, Mo. The value of the diamond drill in all underground explorations by drilling cannot be overestimated.

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[1] The international carat is 0.200 gram.

Problem

A plant is designed to manufacture charcoal from walnut shells which cost $1 per ton. The gas required for charring the shells costs $1 per ton of shells. Electricity is 6 cents per kilowatt-hour and 4¼ hp. of electricity is used continuously per 24-hr. day. Water costs $1.50 per day. Nine tons of shells are used per day to manufacture 3 tons of charcoal. Three men working 10 hr. per day and one man working 8 hr. a day are paid at the rate of 50 cents per hour. Sacking expenses are $4 per ton of charcoal. What is the profit per ton of charcoal selling at $50 per ton?

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CHAPTER X

THE CERAMIC INDUSTRIES

The ceramic industries, also sometimes called the *clay products* or *silicate industries*, have as their finished materials a variety of articles that are essentially silicates. These products may be classified as follows:

1. Whitewares—chinaware, earthenware, pottery, porcelain, stoneware, and vitreous ware.
2. Heavy clay products—common brick, face brick, terra cotta, sewer pipe, and drain tile.
3. Refractories—firebrick, alumina products, silica brick, magnesite brick, chromite brick, silicon carbide refractories, zirconia refractories, aluminum silicate products, olivine products.
4. Enamels and enameled metal.
5. Glass.

The first four of these will be presented later in this chapter; the industry will be dealt with separately in Chap. XII.

The making of pottery is probably the most ancient and one of the most interesting of man's industries; the Chinese and the Egyptians engaged in the art over 6,000 years ago. Museums contain, as a record of man's culture, the clay products produced throughout the ages, many of which have an artistic as well as a utilitarian aspect. Although the essential manufacturing processes used in most of the ceramic industries have remained largely unchanged for a long time, the past 25 years have seen many significant new developments, particularly among refractories.

Uses and Economics.—The value of the pottery produced in the United States in the past decade fluctuated between $40,000,000 and $112,000,000 annually. The present position is around $100,000,000. Table 1 shows certain statistics for the ceramic industry. Brick production varies greatly with the general building program for the country. In 1925 the production of common brick reached 7.6 billions and in 1924 face brick attained 2.5 billions. Both have declined since those maxima. Ohio and Pennsylvania are the chief manufacturing states for the ceramic industries with New Jersey, West Virginia, California, and Missouri following in sequence.

BASIC RAW MATERIALS

The three main raw materials used in making the common ceramic products are (1) clay, (2) feldspar, called *spar* in the industry, (3) sand,

TABLE 1.—U.S. STATISTICS REGARDING CERAMICS[a]

Industry and product	Unit	Quantity (thousands of specified unit)		Value (thousands of dollars)	
		1937	1939	1937	1939
Structural clay products					
Brick and hollow structural tile, total				$64,208	$75,427
Bricks, red burning clays, all sizes	Number	?	4,209,797	?	40,136
Bricks, buff burning clays, all sizes	Number	?	516,082	?	7,090
Glazed units, brick and hollow tile, all sizes	Number	?	194,311	?	5,847
Unglazed structural clay tile:					
Nonload-bearing	Sq. ft.	?	58,109	?	3,251
Load-bearing, backup tile	Sq. ft.	?	72,032	?	5,259
Other					4,244
Terra cotta	Ton	29	28	2,915	2,861
Roofing tile	Square	228	243	2,054	2,376
Floor and wall tile (except quarry tile)	Sq. ft.	64,743	65,672	16,035	16,446
Sewer pipe and kindred products				15,895	18,296
Clay refractories, including refractory cement (clay), total				49,864	40,497
Fire-clay products:					
Brick, block, or tile (except high-alumina)	Number	700,947	507,324	32,806	25,169
Special shapes	Ton	184	152	4,751	3,833
Other				4,981	4,207
Other clay refractories, etc				7,326	7,288
Clay products (except pottery), n.e.c				10,136	10,521
Pottery and related products					
Vitreous-china plumbing fixtures				20,625	22,105
Hotel china				10,018	8,855
Whiteware				25,711	28,237
Porcelain electrical supplies				24,857	20,879
Pottery products, n.e.c				16,174	17,842

[a] U.S. Department of Commerce, "Statistical Abstract of the United States," 1942, p. 882.

called *flint* in the industry. Clays are more or less impure hydrated aluminum silicates that have resulted from the weathering of igneous rocks in which feldspar was a noteworthy original mineral. The reaction may be expressed,

$$\underset{\text{Potash feldspar}}{K_2O \cdot Al_2O_3 \cdot 6SiO_2} + CO_2 + 2H_2O \rightarrow K_2CO_3 + \underset{\text{Kaolinite}}{Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O} + \underset{\text{Silica}}{4SiO_2}$$

There are a number of mineral species called *clay minerals* but the most important are kaolinite, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$; beidellite, $Al_2O_3 \cdot 3SiO_2 \cdot H_2O$; montmorillonite, $Al_2O_3 \cdot 4SiO_2 \cdot H_2O$; and halloysite, $Al_2O_3 \cdot 2SiO_2 \cdot 3H_2O$.

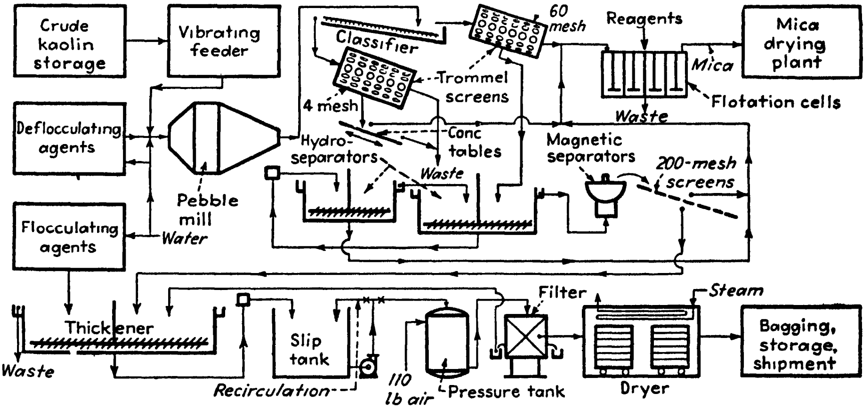
From a ceramic viewpoint clays are plastic and moldable when sufficiently finely pulverized and wet, rigid when dry, and vitreous when fired at a suitably high temperature. Upon these properties depend the manufacturing procedures.

TABLE 2.—BASIC RAW MATERIALS FOR CERAMICS

	Kaolinite	Feldspar	Quartz or flint
Formula	$Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$	$K_2O{\cdot}Al_2O_3{\cdot}6SiO_2$	SiO_2
Plasticity	Plastic	Nonplastic	Nonplastic
Fusibility	Refractory[a]	Easily fusible binder	Refractory[a]
Melting point	3245°F.; 1785°C.	2100°F.; 1150°C.	3110°F.; 1710°C.
Shrinkage on burning	Much shrinkage	Fuses	No shrinkage

[a] Infusible at highest temperature of coal fire (1400°C.).

Accompanying the clay minerals in the clays of commerce are varying amounts of feldspar, quartz, and other impurities such as oxides of iron.



Note: Quantities cannot be given since clay recovery varies from 8 to 18 percent, depending on crude clay used. Plant shown here designed for 30 tons per day output regardless of crude clay variations

FIG. 1.—China clay beneficiation. (*Courtesy of Harris Clay Company.*)

In nearly all the clays used in the ceramic industry, the basic clay mineral is kaolinite, although bentonite[1] clays based on montmorillonite, are used to some extent where very high plasticity is desired. This property of the plasticity[1] or workability of clays is influenced most by the physical condition of the clay and varies greatly among the different types of clay. Clays are chosen for the particular properties desired and are frequently blended to give the most favorable result. Clays vary so much in their physical properties and in the impurities present, that it is frequently

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[1] LEWIS, SQUIRES, and BROUGHTON, "Industrial Chemistry of Colloidal and Amorphous Materials," bentonite, pp. 241–248; plasticity, pp. 453–456, The Macmillan Company, New York, 1942.

necessary to upgrade them by the beneficiation procedure. Figure 1 shows the *steps*[1] necessary for such a procedure wherein sand and mica are removed. The steps in this flow sheet apply almost altogether to the physical changes or *unit operations* such as size separation by screening or selective settling, filtration, and drying. However, the colloidal properties are controlled by appropriate addition agents, such as sodium silicate and alum.

There are three common types of feldspar: potash feldspar, $K_2O \cdot Al_2O_3 \cdot 6SiO_2$; soda feldspar, $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$; and lime feldspar $CaO \cdot Al_2O_3 \cdot 6SiO_2$, all of which are used in ceramic products to some extent. The first is the most common. Feldspar is of great importance as a fluxing constituent in ceramic formulas. It may exist in the clay as mined, or it may be added as needed.

The third main ceramic constituent is sand or *flint.* Its essential properties for the ceramic industries are summarized along with the similar characteristics of clay and feldspar in Table 2. For the light-colored ceramic products, sand with a low iron content should be chosen.

In addition to the three principal raw materials there is a wide variety of other minerals, salts, and oxides that are used as fluxing agents and special refractory ingredients. Some of the more *common fluxing agents* are

Borax, $Na_2B_4O_7 \cdot 10H_2O$
Boric acid, H_3BO_3
Soda ash, Na_2CO_3
Sodium nitrate, $NaNO_3$
Pearl ash, K_2CO_3
Fluorspar, CaF_2
Cryolite, Na_3AlF_6
Iron oxides
Antimony oxides
Lead oxides

Some of the more common *special refractory ingredients* are

Alumina, Al_2O_3
Olivine, $(FeO, MgO)_2SiO_2$
Chromite, $FeO \cdot Cr_2O_3$
Aluminum silicates, $Al_2O_3 \cdot SiO_2$
(cyanite, sillimanite, andalusite)
Dumortierite,
$8Al_2O_3 \cdot B_2O_3 \cdot 6SiO_2 \cdot H_2O$
Magnesite, $MgCO_3$
Lime, CaO, and limestone, $CaCO_3$
Zirconia, ZrO_2
Titania, TiO_2
Hydrous magnesium silicates,
e.g., talc, $3MgO \cdot 4SiO_2 \cdot H_2O$
Carborundum, SiC
Mullite, $3Al_2O_3 \cdot 2SiO_2$

UNIT PROCESSES INCLUDING FUNDAMENTAL CERAMIC CHEMISTRY

All ceramic products are made by combining various amounts of the foregoing raw materials, shaping, and heating to firing temperatures. These temperatures may be as low as 700°C. for some overglazes or as

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[1] SMITH, Deflocculation and Controlled Separation Improve Domestic China Clay, *Chem. & Met. Eng.*, **44**, 594 (1937).

high as 1300 to 1400°C. for many vitrifications. Such temperatures cause a number of reactions which are the chemical bases for the unit processes of

1. Dehydration or "chemical water smoking" at 150 to 650°C.
2. Calcination, *e.g.*, of $CaCO_3$.
3. Oxidation of ferrous iron and organic matter.
4. Silicate formation.

Some of the initial chemical changes are relatively simple, like the calcination of $CaCO_3$ and the dehydrations and decompositions of kaolinite. Other reactions, such as silicate formations, are quite complex and change with the temperature and constituent ratios as depicted by Figs. 2 and 4.

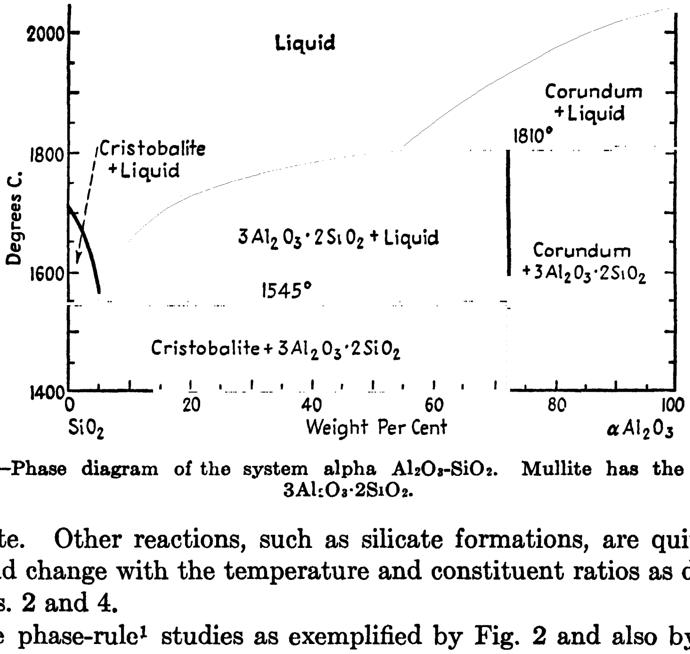

FIG. 2.—Phase diagram of the system alpha Al_2O_3-SiO_2. Mullite has the formula: $3Al_2O_3 \cdot 2SiO_2$.

The phase-rule[1] studies as exemplified by Fig. 2 and also by Fig. 4 have been of *revolutionary importance* in interpreting the empirical observations in the ceramic industries and in making predictions for improvements. For instance, the data of Fig. 2 on the Al_2O_3-SiO_2 system have led to the important development of processes for mullite refractories (see page 180). This diagram shows that any percentage of liquefaction can be obtained, dependent on a definite temperature, except at the monovariant points. Thus, if the progressive melting be kept from going too far by controlling the rise in temperature, sufficient solid skeletal material will remain to hold the hot mass together. This Al_2O_3-SiO_2 diagram shows that mullite is the only stable compound of alumina and silica at high temperature.

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[1] BIRCH, Phase-equilibrium Data in the Manufacture of Refractories, *J. Am. Ceram. Soc.*, **24**, 271 (1941); HALL and INSLEY, A Compilation of Phase Rule Diagrams of Interest to the Ceramist and Silicate Technologist, *J. Am. Ceram. Soc.*, **16**, 455–567 (1933).

Being primarily silicates, ceramic products are all more or less refractory, *i.e.*, resistant to heat, and the degree of refractoriness of a given product is determined by the relative quantities of refractory oxides and fluxing oxides. The principal refractory oxides are SiO_2, Al_2O_3, CaO, and MgO, with ZrO_2, TiO_2, Cr_2O_3, and BeO used less commonly. The principal fluxing oxides are Na_2O, K_2O, B_2O_3, and SnO_2, with fluorides also used as fluxes in certain compositions.

The essential ingredient of all ceramic products is clay (kaolinite, usually) and therefore the chemical reactions which occur on heating clay are quite important. The first effect of the heat is to drive off the water of hydration which occurs at around 600 to 650°C. and which absorbs much heat, leaving an amorphous mixture of alumina and silica, as shown by X-ray studies.

$$\mathrm{Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O} \rightarrow \mathrm{Al_2O_3} + 2\mathrm{SiO_2} + 2\mathrm{H_2O}$$

In fact a large proportion of the alumina can be extracted with hydrochloric acid at this stage. As heating is continued, the amorphous alumina changes quite sharply at 940°C. to a crystalline form of alumina, gamma alumina, with the evolution of considerable heat. At a slightly higher temperature, beginning at about 1000°C., the alumina and silica combine to form mullite, $3Al_2O_3{\cdot}2SiO_2$. At a still higher temperature, the remaining silica is converted into crystalline cristobalite. Therefore the fundamental over-all reaction in the heating of clay is as follows:

$$\underset{\text{Kaolinite}}{3(\mathrm{Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O})} \rightarrow \underset{\text{Mullite}}{3\mathrm{Al_2O_3{\cdot}2SiO_2}} + \underset{\text{Cristobalite}}{4\mathrm{SiO_2}} + 6\mathrm{H_2O}$$

The equilibrium state of Al_2O_3-SiO_2 mixtures as a function of temperature is summarized in the phase equilibrium diagram of this system shown in Fig. 2. The presence of fluxes tends to lower the temperature of formation of mullite and of attainment of the equilibrium conditions reported in the equilibrium diagram.

An actual ceramic body contains many more ingredients than clay itself. Hence the chemical reactions are more involved, and there will be other chemical species besides mullite and cristobalite present in the final product. For example, various silicates and aluminates of calcium, magnesium, and possibly the alkali metals might be present. However, the alkali portion of feldspar and most of the fluxing agents become a part of the glassy or vitreous phase of the ceramic body. All ceramic bodies undergo a certain amount of vitrification or glass formation during heating and the degree of vitrification depends upon (1) the relative amounts of refractory and fluxing oxides in the composition, (2) the temperature, and (3) the time of heating. The vitreous phase imparts desirable properties to some ceramic bodies, *e.g.*, acting as a bond and imparting translucency in chinaware. Even in refractories some vitrification is desirable to act as a bond but extensive vitrification would destroy the refractory property. Thus it is seen that any ceramic body is composed of a vitreous matrix plus crystals, of which mullite and cristobalite are two of the most important.

The *degree of vitrification* provides the basis for a useful classification of ceramic products as follows:

1. Whitewares.
   Varying amounts of fluxes, heat at moderately high temperatures, varying vitrification.
2. Heavy clay products.
   Abundant fluxes, heat at low temperatures, little vitrification.
3. Refractories.
   Little fluxes, heat at high temperatures, little vitrification.
4. Enamels.
   Very abundant fluxes, heat at moderate temperatures, complete vitrification.
5. Glass.
   Moderate fluxes, heat at high temperatures, complete vitrification (see Chap. XII).

WHITEWARES

The whitewares include chinaware, earthenware, pottery, porcelain, stoneware, and vitreous ware. These are based on selected grades of clay bonded together with varying amounts of fluxes and heated to a moderately high temperature in a kiln (1200 to 1500°C.). Because of the different amounts and kinds of fluxes there is a corresponding variation in the degree of vitrification among the whitewares from earthenware to vitrified china. These may be broadly defined as follows:

Earthenware[1] is "a porous nontranslucent ware with a soft glaze." Earthenware is sometimes called *semivitreous* dinnerware.

Chinaware[1] is "a commercially vitrified translucent ware with a medium glaze which resists scratching to a greater or less degree."

Porcelain[1] is "a thoroughly vitrified, translucent ware with a hard glaze which resists scratching to the maximum degree." This includes dinnerware but also the exceedingly important insulation porcelain so essential in the electrical field.

Stoneware especially chemical stoneware[2] is closely related to porcelain. The stoneware may be regarded as a crude porcelain, the raw materials being of poorer grade and the manufacturing not so carefully carried out.

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[1] WATTS, The Selection of Dinnerware for the Home, *Circ.* 21, 3d ed., Eng. Exp. Station, Ohio State University, Columbus, 1940; Classification of Ceramic Dinnerware, *Bull. Am. Ceramic Soc.*, **16**, 246–47 (1937).

[2] Pictured flow sheet, *Chem. & Met. Eng.*, **47**, 637 (1940).

Pottery is usually a broad classification including earthenware, china, and porcelain.

Detailed presentations of the different kinds of whiteware should be sought in the specialized books to which reference is given at end of this chapter. To represent the typical manufacturing procedures in this group, porcelain is chosen.

Manufacture of Porcelain.—There are three lines of production: (1) the *wet process porcelain* used for production of fine-grained highly glazed insulators for high-voltage service, (2) the *dry process porcelain* employed for rapid production of more open-textured low-voltage pieces, and (3) the *cast porcelain* necessary for the making of pieces too large or too intricate for the other two methods. These three processes are based on the same raw materials, the differences in manufacturing being largely in the drying and forming (shaping) steps. The wet process is illustrated[1] by Fig. 3. This flow sheet may be broken down into the following sequences of *unit operations* (Op.) and *unit processes* (Pr.):

The raw materials of proper proportions and properties to furnish porcelain of desired quality are weighed from overhead hoppers into the weighing car (Op.).

The feldspar, clays, and flint are mixed with water in the blunger (clay-water mixer) and then passed over a magnetic separator, screened, and stored (Op.).

Most of the water is removed (and wasted) in the filter press (Op.). All the air is taken out in the pug mill assisted by vacuum and slicing knives. This results in a denser and stronger porcelain (Op.).

The prepared clay is formed into blanks in a hydraulic press or by hot pressing in suitable molds (Op.).

The blanks are preliminarily dried, trimmed, and finally completely dried—all under carefully controlled conditions (Op.).

A high surface luster is secured by glazing with selected materials (Op.).

The vitrification of the body and the glaze is carried out in tunnel kilns with exact controls of temperature and movement (Pr.).

The porcelain articles are protected by being placed in saggers[2] fitted one on top of the other in the cars. This represents a one-fire process wherein body and glaze are fired simultaneously. The porcelain pieces are rigidly tested electrically and inspected before storage for sale (Op.).

Much *tableware* is manufactured by more complicated procedures than illustrated by the somewhat related porcelain product. Some objects are shaped by "throwing" on the potter's wheel by skilled hands working the revolving plastic clay into the desired form; some objects are "cast" from the clay slip in molds of absorbent plaster of paris. After drying, the latter are removed and further processed. Mass production of simple round objects like cups, saucers, or plates, is carried out economically by "jigging" where the plastic clay is pressed into or on a single revolving mold, the potter often being aided in shaping the other surface and in removing excess clay by a lever which he lowers over the mold, shaped in the profile of the object desired. The mold is placed in the drying room.

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[1] Pictured flow sheet, *Chem. & Met. Eng.*, **46**, 421 (1939).

[2] Saggers are made by mixing coarse granules obtained from grinding old saggers with new clay and water in a pug mill and discharging the doughlike mass from an extrusion machine in loaf form. These loaves are placed in a molding machine, where box shape is imparted, and then fired. They may be used several times.

The vitrification as shown in Fig. 3 is by the one-fire process. Frequently the two-fire method is used wherein the body is fired, cooled, glazed, and fired again.

Glazing is always important in whitewares; it is particularly so for tableware. A glaze is a thin coating of glass that is melted onto the surface of the more or less porous ceramic ware. It contains ingredients of two distinct types in different proportions: (1) refractory materials, such as feldspar, silica, and china clay and (2) fluxes, such as soda, potash, fluorspar, and borax. Different combinations of these materials and different temperatures at which they are fired give a wide range of texture and quality. The glaze must bond with the ware, and its coefficient of expansion must be sufficiently close to that of the ware to avoid defects such as "crazing" and "shivering." The glaze may be put on by dipping, spraying, pouring, or brushing. All of these methods need a great deal of care. Decorations may be applied by carving, painting with a thick paint, marbling (dabbing on paint), tracing with a glass tube, or combing. For high-grade tableware, the decorations are by decalcomania paper which is simply a mechanical means for manifold duplication of the same design. However, such designs are "touched up" by an artist. For the highest type of tableware much hand decorating is practiced. Decoration of such ware may be "underglaze" or "overglaze."

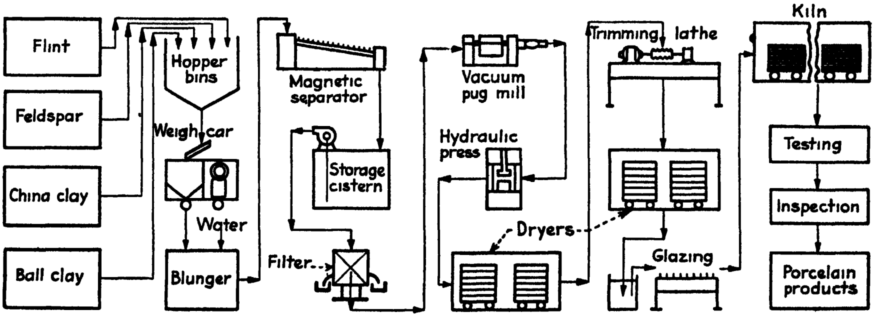

FIG. 3.—Porcelain manufacture by the wet process of Westinghouse.

Glost firing is the technical term for the firing of the glaze. Care should be taken in packing the kiln or the saggers so that the ware does not touch except for the three necessary underneath supports. As much space as practical is allowed between the different pieces of the wares since the glazes often bubble and rise before flattening. The temperature of the glost kiln may be increased more rapidly than during the first firing, but heating should not be hurried as strains would be set up. Large shapes should be packed in the center of the kiln to avoid uneven heating and should be fired more slowly than small ones. Earthenware should be glazed between 1050 and 1100°C.; stoneware between 1250 and 1300°C.

HEAVY CLAY PRODUCTS

Low-cost but very durable products, such as common brick, face brick, terra cotta, sewer pipe, and drain tile, are frequently manufactured from the cheapest of common clays with or without any glazing. The clays used generally carry sufficient impurities to provide the needed fluxes for binding. When glazed, as in sewer pipe or drain tile, this may be done by throwing salt ("salt glaze") upon the kiln fire. The volatilized salt forms the fusible coating or glaze.

Manufacture of Building Brick.—One of the most important of clay products is building brick, which comprises common and face brick. The raw materials are clays from three groups: (1) red burning clay, (2) white burning clay, (3) buff burning clay, usually a refractory. The requirements for a face-brick clay are freedom from warping, absence of soluble salts, sufficient hardness when burned at a moderate temperature, and general uniformity in color upon burning. Requirements for common brick are much less stringent. Red burning clay is most used for both common and face brick; however, the semirefractory buff-colored clay is in great demand because coloring matter may be added to vary the color effects. Manganese, with white or buff burning clay, gives a very attractive color.

Bricks are manufactured by both the *soft-mud* and the *stiff-mud* methods. The soft-mud procedure consists in molding the clay containing 20 to 25 per cent water in brick molds coated with a thin layer of sand to facilitate removal. The molded brick is then burned. Such bricks are of a uniform and excellent quality with good edges. This soft-mud process is much employed for firebrick and is the ancient method for making building bricks. In the modern stiff-mud procedure the clay is wet only enough (10 to 12 per cent) to stick together when worked. This clay is then forced out through a die in an auger machine. The extended bar of stiff clay is cut by wires to form the bricks. These bricks (as well as those from the soft-mud process) may be repressed to make face brick. This repressing not only ensures a more uniform shape but overcomes the internal stress set up by the extrusion in the auger machine. These molded bricks may be stacked 6 to 10 ft. high without damage before being dried.

The stiff-mud process is employed for the manufacture of practically *every clay product including all types of brick, sewer pipe, drain tile, hollow tile, refractories, fireproofing, and terra cotta. The clay in some* cases can be worked directly from a bank into the stiff-mud machine, but a more desirable product will result if the clay is ground and tempered before being used. The greater percentage of clay ware is made by the stiff-mud process.

Bricks are *dried* in various ways: outdoors, in sheds, or in tunnel driers. After drying, the bricks are *fired* in kilns of such type as described later in the chapter, to a temperature from 875 to somewhat above 1000°C.

REFRACTORIES

Refractories[1] embrace those materials which are used to withstand the effect of thermal, chemical, and physical effects that are met with in furnace procedures. Refractories are sold in the form of firebrick, silica brick, magnesite brick, chromite brick, silicon carbide refractories, zirconia refractories, aluminum silicate products, olivine products, and others. The variety of refractories available is increasing, thus enabling a better selection of a refractory for a particular use. In making refractories the main material is chosen to adapt itself best to the thermal, chemical, and mechanical conditions to be met with. The fluxes required to bind together the particles of the refractories are kept at a minimum. Largely because of this there is but little vitrification.

Properties of Refractories.—In determining the refractory best suited for a definite operation it is necessary to consider the working temperature of the furnace where the refractory is needed, the rate of temperature change, the load applied during heats, and the chemical reactions that are encountered. Generally, several types of refractories are required for the construction of any one furnace because no single refractory can withstand all the different conditions that prevail in the various parts of the furnaces. In order to guard against reaction between the bricks of different kinds a separating cement or brick that has little tendency to react with either of the adjacent refractories should be used.

Chemical Properties.—The usual classification of commercial refractories divides them into acid, basic, and neutral groups, although in many cases a sharp distinction cannot be made. Silica bricks are decidedly acid, and magnesite bricks are strongly basic; however, fire-clay bricks are generally placed in the neutral group though they may belong to either of these classes depending upon the relative silica-alumina content. Also, in the alumina-silica series of refractories many types can be made with wide differences in their chemical reactions. It is usually inadvisable to employ an acid brick in contact with an alkaline product, or vice versa. Neither chemical reactions nor physical properties are sole criteria of acceptable behavior; both should be considered. Chemical action may be due to contact with slags, fuel ashes, and furnace gases as well as with products such as glass or steel. Among the gases that have a deleterious effect are carbon monoxide, sulfur dioxide, natural gas, hydrogen, and steam.

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[1] NORTON, "Refractories," 2d ed., McGraw-Hill Book Company, Inc., New York, 1942. This volume is most essential for everyone working in this field particularly, because of the hundreds of classified references to further details in the literature.

TABLE 3.—FUSION TEMPERATURES OF REFRACTORIES[a]

Material	Temperature, °C.	Temperature, °F.
Fire-clay brick	1500–1750	2732–3182
Kaolinite, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	1785	3245
Silica brick	1700	3090
Silica, SiO_2	1710	3110
Bauxite brick	1732–1850	3150–3362
High-alumina clay brick	1802–1880	3276–3416
Mullite, $3Al_2O_3 \cdot 2SiO_2$	1810	3290
Sillimanite, Al_2SiO_5	1816	3300
Forsterite, $2MgO \cdot SiO_2$	1890	3434
Chromite, $FeCr_2O_4$	2180	3956
Chrome brick	1950–2280	3542–3992
Alumina, Al_2O_3	2050	3722
Spinel, $MgO \cdot Al_2O_3$	2135	3875
Silicon carbide brick	2200 decompn.	3992 decompn.
Magnesite brick	2200	3992
Zirconia brick	2200–2700	3992–4892

[a] NORTON, "Refractories," pp. 399–403, McGraw-Hill Book Company, Inc., New York, 1942. For other data on refractory materials, see PERRY, *op. cit.*, pp. 2154–2157.

Porosity.—The porosity is directly related to many other physical properties of the brick including their resistance to chemical attack. The higher the porosity of the brick the more easily it is penetrated by molten fluxes and gases. For a given class of brick the one with lowest porosity has the greatest strength, thermal conductivity, and heat capacity.

Fusion Point.—Before use, the softening point of a refractory should be determined. It is found by use of pyrometric cones of predetermined softening points. Most commercial refractories soften gradually over a wide range and do not have sharp melting points because they are composed of several different minerals both amorphous and crystalline in type. The pyrometric cones (once known as *Seger* cones) are small pyramids made of mixtures of oxides and are useful for the approximate measurement of temperatures by steps averaging about 36 deg. from 1100 to 3700°F. These are considered indispensable, not because of high temperature accuracy but because their temperature–time performance is similar to that of the materials being fired. The fusing points of these pyrometric cones are available in the literature.[1] Typical fusion points of refractories, both for pure substances and for technical products, are given in Table 3.

Spalling.—A fracturing or a flaking off of a refractory brick or block due to uneven heat stresses or compression caused by heat is known as *spalling.*[2] Refractories usually expand when heated. Bricks with the highest expansion and least uniform rate are most susceptible to spalling when subjected to rapid heating and cooling. When refractories are heated for a great length of time at high temperatures, they may have a permanent volume change, either expansion or contraction, which may be caused by mineral inversion, softening, or overfiring.

Strength.—Cold strength usually has only slight bearing on strengths at high temperatures. Although most of the applications place refractories under compressive loads, in rare cases they may be subjected to tension or shear alone. Resistance to abrasion or erosion is also very important for many furnace constructions such as by-product coke-oven walls, and linings of the discharge end of rotary cement kilns.

Resistance to Rapid Temperature Changes.—Generally speaking, bricks with the lowest thermal expansions and coarsest textures are most resistant to rapid thermal change; less strain develops also. Bricks that have been used for a long time are usually altered in their properties, often being melted to glassy slags on the outside surface or even being more or less corroded away.

Thermal Conductivity.—The densest and least porous bricks have the highest thermal conductivity, owing to absence of air in voids. Though heat conductivity is wanted in some furnace constructions, as in muffle walls, it is not so desirable as some other properties of the refractories such as resistance to firing conditions and is given minor consideration. Insulation is desired in special refractories.

Heat Capacity.—Furnace heat capacity depends upon the thermal conductivity, the specific heat, and the specific gravity of the refractory. The low quantity of heat absorbed by lightweight brick works as an advantage when furnaces are operated intermittently because the working temperature of the furnace can be obtained in less time with less fuel. Conversely, the dense and heavy fire-clay brick would be best for regenerator checkerwork, as in coke ovens, glass furnaces, and stoves for blast furnaces.

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[1] A.S.T.M. Designation: C24-42. Many other specifications for refractories and refractory materials are given in the A.S.T.M. standards. See PERRY, *op. cit.*, p. 2066.

[2] NORTON, *op. cit.* Chapter XIV is devoted entirely to spalling with many literature references.

Manufacture of Refractories.—The usual methods for manufacturing refractories include these *unit operations* and *unit processes:* (1) grinding and screening, (2) mixing, (3) pressing or molding and repressing, (4) drying, and (5) burning or vitrification. Usually the most important single property to produce in manufacture is high bulk density, which affects many of the other important properties such as strength, volume stability, slag, and spalling resistance, as well as heat capacity. On the other hand, for insulating refractories a porous structure is required, which means a low density.

Grinding.—Obviously, one of the most important factors is the size of the particles in the batch. It is known that a mixture in which the proportion of coarse and fine particles is about 55 to 45, with only few intermediate particles, gives the densest mixtures. Careful screening, separation, and recycling are necessary for close control. This works very well on highly crystalline materials but is difficult to obtain in mixes of high plasticity.

Mixing.—The real function of mixing is the distribution of the plastic material so as to *coat* thoroughly the nonplastic constituents. This serves the purpose of providing a lubricant during the molding operation and permits the bonding of the mass with minimum voids.

Molding.—The great demand for refractory bricks of greater density, strength, volume, and uniformity has eventually resulted in the adoption of the dry-press method of molding with mechanically operated presses and the discarding of hand molding and extruding processes. The dry-press method is particularly suited for batches that consist primarily of nonplastic materials. In order to use high-pressure forming it is necessary to deair the bricks during pressing to avoid laminations and cracking when the pressure is released. There are four ways of deairing dry-press bricks: (1) Decreasing the rate of pressure application and release so that the air in the voids has opportunity to seep through the sides of the brick and mold box. (2) Double pressing of the materials. In this method the bricks are pressed and allowed to crack. Repressing then closes the cracks. (3) Deairing by use of a gas, such as butane, which is piped to the mold box to displace the air. When pressure is applied, the gas is absorbed by the clay or condensed. If a flammable gas is used, it should be more carefully handled to reduce the fire hazard. (4) The use of a vacuum applied through vents in the mold box. This has been used successfully and seems to hold the most promise (*cf.* vacuum pug mill in Fig. 3). Large special shapes are not adapted to machine molding; however, their manufacture has been improved by the use of tamping with pneumatic tools to attain very high densities.

Drying.—Drying is used to remove the moisture that was added before molding to develop plasticity. It should be noted that the elimination of water leaves voids and causes high shrinkages and internal strains. For this reason the dry-press process (requiring only 5 to 8 per cent of moisture, instead of 10 to 15 per cent in the stiff-mud method) has been favored in the manufacture of practically all types of refractory materials. In some cases drying is omitted entirely and the small amount necessary is accomplished during the heating stage of the firing cycle.

Burning.—Burning may be carried out in the typical round downdraft kilns or continuous tunnel kilns. Two important things take place during burning: (1) the development of a permanent bond by a *partial vitrification* of the mix and (2) the development of the stable mineral forms for future service as shown in the phase diagrams of Figs. 2 and 4. The changes that take place are the removal of the water of hydration and, then, the calcination of carbonates and the oxidation of ferrous iron. During these changes, the volume may shrink as much as 30 per cent, and severe strains are set up in the refractory. This shrinkage may be eliminated by the *prestabilization* of the materials used. There are commercial refractories (see Unburned Refractories, page 181) in which the burning operation is entirely eliminated because the raw materials are prestabilized, appropriately sized, and pressed.

Varieties of Refractories.—As yet no one refractory brick has been made that will be suitable under all conditions. Although a refractory is usually thought of in terms of its ability to withstand temperature, it is really only in exceptional cases that heat is the sole agent that effects the final destruction. Hence, the need for different refractories.

Fire-clay Brick.—Fire clays are the most widely used of all the various refractory materials as they are well suited for a wide variety of applications and may be obtained in almost any quantity. Fire clays range in chemical composition from those containing a large excess of free silica to those which have a high-alumina content. As would be expected for material with such wide variation in quality and raw materials, there is a considerable spread in price of firebricks from $35 to $50 per M.

The steel industries are the largest consumers of refractories in the linings of blast furnaces, stoves, open hearths, and other furnaces. Other industries having use for these are foundries, limekilns, pottery kilns, cupolas, brass and copper furnaces, continuous ceramic and metallurgical kilns, boilers, gas-generating sets, glass furnaces, carbon furnaces, and heat-treating furnaces.

High-alumina Refractories.—High-alumina refractories have come into wide use only in the past 15 years. The demand for these as bricks is largely due to the improvements in the quality and to the growing demand for refractories that can withstand severe conditions for which fire-clay and silica bricks are not suitable. High-alumina bricks are really high-alumina clay bricks. The refractoriness and the temperature of incipient vitrifaction increase with the alumina content. Another *valuable property of high-alumina bricks is that they are practically inert to carbon monoxide and are not disintegrated by natural gas* atmospheres up to 1000°C. Their price varies directly with the alumina content and ranges from $75 to $300 per M.

The cement industry is the largest user of high-alumina brick. Another successful application of these is in the calcining zones of rotary lime and dolomite kilns such as are employed in the calcining of the lime sludge in sulfate paper mills. They have proved successful in boiler settings because of the resistance to the chemical action of fuel ash which contains basic oxides. They have proved economical for the linings of glass furnaces, oil-fired furnaces, high-pressure oil stills, in the roofs of lead softening furnaces, crowns of silicate of soda furnaces, and in regenerator checkers of blast furnaces.

Almost pure alumina in the form of sintered corundum is meeting an exacting need for aviation spark plugs.

Silica Brick.—Silica bricks contain about 95 to 96 per cent SiO_2 and about 2 per cent of lime added during grinding to furnish the bond. Silica bricks have a permanent expansion which occurs during firing and which is caused by an allotropic transformation that takes place in the crystalline mass. When reheated, silica bricks again expand about 1.5 per cent. This fact should be considered in their use. Silica bricks are manufactured in many standard sizes by power pressing. They have a very homogeneous texture free from air pockets and molding defects. The low porosity is a highly desirable property for the resistance to slag penetration. The price is around $45 per M.

The physical strength of silica bricks is much higher than for those made from clay. For this reason they are used in arches in large furnaces. Furnaces using these must be heated and cooled gradually to lessen spalling and cracking. Open-hearth furnaces have silica bricks in their main arch, side walls, port arches, and bulkheads. In glass furnaces the arches and sides are silica also. Because of their high thermal conductivity silica bricks have been utilized in by-product coke ovens and gas retorts. Other uses are in electrical furnaces, Bessemer converters, and copper-smelting reverbatory furnaces.

Magnesite Brick.—Magnesite bricks are among the most important of the basic refractories. They contain about 85 per cent MgO and about 7 per cent Fe_2O_3 which react to give the proper bond. Their fusion point is higher than that of any other commercial refractory (3900°F.), and the cold strength is very high. These bricks do not stand much load at elevated temperatures but crack and spall very easily when subjected to changes in temperature. Whereas the thermal expansion is relatively high, it decreases with rise in temperature. Magnesite bricks are very expensive and, therefore, are used only to withstand a basic reaction and when supported with metal. These bricks cost from $320 to $350 per M. The largest use for these is in open-hearth furnaces, although many are employed for lining copper converters and for the construction of parts of copper reverberatory and refining furnaces. Some unusual applications are in the crucibles and walls of carbon bisulfide furnaces, rotary lime-sludge kilns, and litharge furnaces.

Chromite Brick ($FeO{\cdot}Cr_2O_3$).—Chromite is sometimes classified as a basic material though it is neutral in its chemical reaction. Recent improvements in the method of manufacture of chrome bricks have provided greater strength and greater spalling resistance at high temperature. Bricks made from this refractory find but little use outside the steel industry. Their cost is from $230 to $250 per M.

Silicon Carbide Refractories.—These are classed among the superrefractories. Such refractories are noted for their ability to withstand sudden changes in temperature, and they are also resistant to many chemical reagents. In their manufacture the crude material from the silicon carbide furnace is ground and the ceramic bond is added. The bond may be finely divided silicon carbide itself, in some cases, or clay. This mixture is then molded to shape and the bond vitrified. In the higher grades less than 10 per cent of bonding material is employed. These bricks are extremely refractory and possess a high thermal conductivity, low expansion, and high resistance to abrasion and spalling. They are strong mechanically and they withstand loads in furnaces to temperatures as high as 1650°C. At higher temperatures this strength is less.

These refractories are used chiefly in muffles because of their thermal conductivity. Their ability to absorb and release heat rapidly and their resistance to spalling under repeated temperature changes make them desirable for recuperators. Refractories of this type can be made thinner than those from fire clay.

Zirconia Refractories.—These are among the most heat resisting of refractories. They are made by grinding 20 per cent of the zirconia ore to pass a 200-mesh screen. This fine material becomes colloidal when mixed with water and, consequently, is employed as the bond. The refractories are then dry-pressed and burned. As pure zirconium oxide fuses at approximately 2700°C. (4892°F.), this material has an excellent foundation for a furnace refractory, but the expense of mining and the fact that the ZrO_2 content is usually low have prevented any extensive development.

Refractories from Crystalline Aluminum Silicates.—Refractories that contain a high percentage of crystalline mullite ($3Al_2O_3{\cdot}2SiO_2$) are called *mullite* refractories. Fire-clay refractories at temperatures around 1600°C. tend to become viscous and are not suitable to carry loads. Since mullite remains in the crystalline state at this and higher temperatures (Fig. 2), there has been a search for aluminum silicate minerals that can be converted to nearly 100 per cent mullite. Among the minerals used are cyanite,[1] sillimanite, andalusite, and dumortierite. Of these the most promising and the largest used is cyanite. The good electrical resistance makes this refractory well suited for electrical equipment.

Electrocast Refractories.[2]—The electrocast refractories are manufactured by introducing a mixture of diaspore clays of high-alumina (to furnish $3Al_2O_3{\cdot}2SiO_2$ ratio) content into the top of an electrical furnace. If necessary, these are adjusted to furnish the stable mullite ratio of $3Al_2O_3{\cdot}2SiO_2$. Molten aluminum silicate at 3400°F. is tapped from the furnace at intervals and poured into molds built from sand slabs. The molds containing these blocks are then annealed from 6 to 10 days before the blocks are removed for use. The refractory obtained from this process has a vitreous, nonporous body which shows a linear coefficient of expansion of about one-half that of good firebrick. The blocks cannot be cut or shaped but may be ground on Alundum wheels; however, skill in casting has progressed rapidly and now many sizes and intricate shapes are being made successfully. This electrocast mullite has only 0.5 per cent voids in contrast with the usual 17 to 29 per cent voids in fire-clay blocks. Cast refractories called *Corhart* blocks are used in glass furnaces, as lining of hot zones of rotary kilns, in modern boiler furnaces exposed to severe duty, and in metallurgical equipment such as forging furnaces. The refractories have the advantages of long life and minimum wear, against which must be balanced their greater initial cost.

Olivine Refractories.—The natural occurring mineral, olivine,[3] contains $2(Mg,Fe)O{\cdot}SiO_2$ and is a silicate characterized by its refractoriness. In the manufacture of refractories from this, dead-burned magnesite is usually added to convert some accessory minerals to fosterite, Mg_2SiO_4, which is the most stable magnesium silicate at high temperatures as shown by Fig. 4. For example, enstatite (or clinoenstatite of Fig. 4) occurring in the rock olivine as mined, is converted to forsterite,

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[1] Cyanite, andalusite, and sillimanite change to mullite and silica when strongly heated. All three have the empirical composition represented by Al_2SiO_5. Dumortierite is a basic aluminum borosilicate. All of them are of great importance in the manufacture of spark plugs, an example of a highly specialized but very essential refractory.

[2] SCHROEDER, Electric Furnace Production of High Heat Duty Refractories, *Ind. Eng. Chem.*, **23**, 124 (1931).

[3] GOLDSCHMIDT, Olivine and Fosterite Refractories in Europe, *Ind. Eng. Chem.*, **30**, 32–34 (1938); HARVEY and BIRCH, Olivine and Fosterite Refractories in America, *Ind. Eng. Chem.*, **30**, 27–32 (1938).

$$\underset{\text{Enstatite}}{MgO\cdot SiO_2} + \underset{\text{Magnesia}}{MgO} \rightarrow \underset{\text{Forsterite}}{2MgO\cdot SiO_2}$$

Such refractories have the advantages of a high melting point, no transformations during heating, and unsurpassed volume stability at high temperatures. No calcining is necessary in their preparation. These refractories have been used successfully for copper-refining furnaces and as mortar for the joining of other refractory bricks.

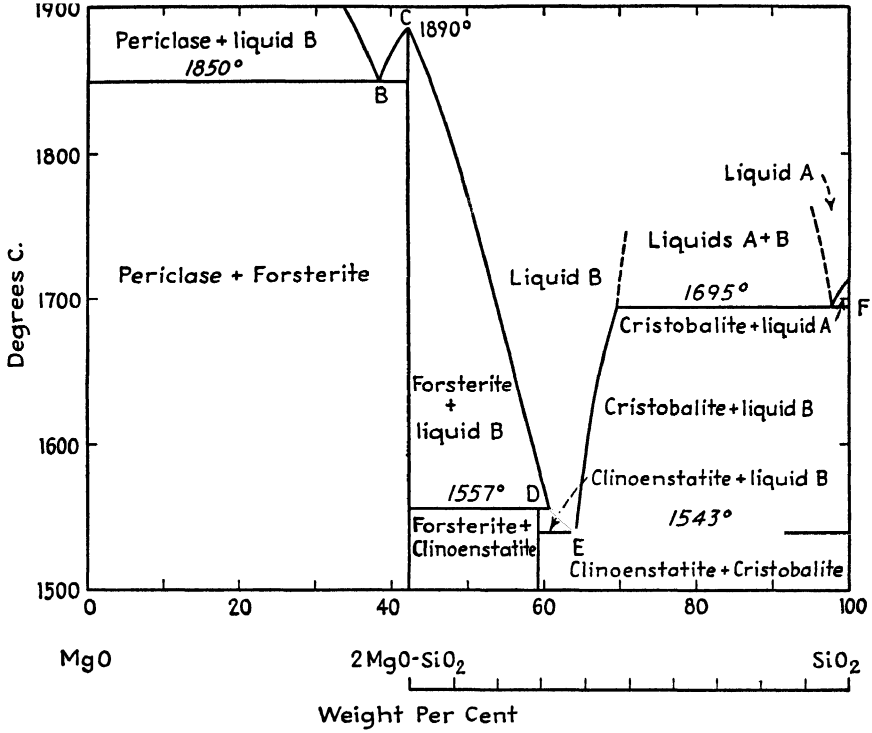
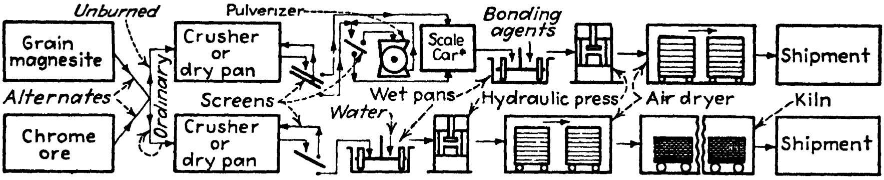


FIG. 4.—Phase diagram of the system MgO-SiO$_2$. [*From Hall and Insley, J. Am. Ceram. Soc.*, **16**, 493 (1933).]

Unburned Refractories.—The disadvantages of lack of bond and volume stability in unburned bricks have been overcome by three distinct improvements in the manufacturing process: (1) Interfitting of grains has been developed to a maximum by using only selected particle sizes combined in the proper proportions to fill all the voids. (2) The forming pressure has been increased to 10,000 lb. per sq. in. and deairing equipment used to reduce the voids between the grains. (3) The use of a refractory chemical bond. The flow sheet for the manufacture of unburned refractories is shown in Fig. 5.

The bricks produced are known as *Ritex*[1] refractories, and both a magnesite and a chrome brick are now in commercial production. These bricks have a higher density and, therefore, better slag-resisting properties than burned brick, and an outstanding resistance to spalling.

Insulating Brick.—Insulating bricks are of two types: (1) for backing of refractory bricks and (2) in place of regular refractory bricks. Most bricks used for backing are made from naturally porous diatomaceous earth, while the second type, usually called *lightweight* refractories, are similar in composition to heavy bricks and owe their insulating value to the method of manufacturing. For instance, waste cork is ground and sized; this is mixed with the fire clay, molded, and burned. In the kiln the cork burns out leaving a highly porous and light brick. These lightweight refractories may be used safely for temperatures of 2500 to 2900°F., while diatomaceous earth brick are not suitable above 2000°F. under ordinary conditions.



*Selected grain sizes are screened out and recombined in definite proportions for maximum density. It has been found that a suitable proportion for many purposes is 55 parts of coarse to 45 parts of fine particles, with elimination of intermediate sizes.

Unburned refractories made by several manufacturers; process shown is that of General Refractories Co.

FIG. 5.—Flow chart for unburned refractories by Ritex process, compared with burned brick process. (*Courtesy of General Refractories Company.*)

ENAMELS AND ENAMELED METAL

Porcelain or vitreous enamel is a ceramic mixture containing a large proportion of fluxes, applied cold and fused to the metal at a moderate red heat. *Complete vitrification* takes place. The application of enamels to metals is one that dates back to the ancients. Various pieces of gold, silver, and copper enamelware, as well as of enameled earthenware, are in existence from the ancient Egyptian, Greek, and Byzantine nations. Commercial enameling on iron was started in Czechoslovakia in 1830 and in the United States about 1867. The use of porcelain enamels on many different articles has spread tremendously especially in the United States where borax is cheap and abundant. Signs, table tops, restaurant equipment, stoves, refrigerators, wash tubs, bathtubs, and other porcelain and enamel products have found a wide market. Porcelain enamel, long valued as a material of great beauty in the field of decorative art, is coming more and more into general commercial use because it provides a product of great durability and one applicable to a wide range of uses. It is easy to clean and resists corrosion. Glass enameled steel for chemical use has become one of the indispensable tools of the chemical engineer.

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[1] TROSTEL, Recent Developments in Manufacturing and Using Refractories, *Chem. & Met. Eng.*, **42**, 363 (1935).

Raw Materials.—Raw materials for enamels must have not only high purity but also fineness, suitable mineral composition, proper grain shape, and other physical conditions depending on the specific enamel. The raw materials used in enamels may be divided into six different groups: refractories, fluxes, opacifiers, colors, floating agents, and electrolytes. The *refractories* include such materials as quartz, feldspar, and clay which contribute to the acidic part of the melt and give body to the glass. The *fluxes* include such products as borax, soda ash, cryolite, and fluorspar, which are basic in character and *react* with the acidic refractories to form the glass. They tend to lower the fusion temperatures of the enamels.

The *opacifiers* are compounds added to the glass to give it the white opaque appearance so characteristic of vitreous enamels. They are of two principal types: insoluble opacifiers (tin oxide, antimony oxide, sodium antimonate, and zirconium oxide) and devitrification opacifiers (cryolite and fluorspar). The latter type also act as fluxes rendering the enamel more fusible. The *color* materials may be oxides, elements, salts, or frits and may act either as refractories or as fluxes. The color contributed to an enamel may be influenced by the enamel composition and the processing.

The *floating agents* such as clay and gums are chosen to suspend the enamel in water or in some other liquid. Many different varieties of clay are used, but a plastic clay quite free from impurities is required. To peptize the clay and properly suspend the enamel, *electrolytes* are added. These are such compounds as borax, soda ash, magnesium sulfate, and magnesium carbonate, which, when added in very small amounts, aid the clay in keeping the enamel in suspension.

Manufacture of the Frit.—The preparation of the enamel glass, or frit, is similar to the first stages of the manufacture of ordinary glass. The raw materials are mixed in the proper proportions and charged into a melting furnace maintained near 2500°F., from 1 to 3 hr., depending upon the composition of the enamel and the size of the mixture. After the batch has been uniformly melted, it is allowed to pour from the furnace into a tank of cold water. The contact with the cold water in the quenching tank shatters the melt into millions of friable pieces. This is called *frit*.

This frit is now ground in a ball mill containing balls of dense white porcelain; then the opacifying material is charged and the coloring oxides, the clay and more frit, and lastly the water. The fineness of the grinding depends upon the nature of the metal surface to which the enamel is to be applied. The product from the mill is discharged and passed through a 60- or 80-mesh screen to eliminate any oversized particles. The enamel slip is aged at temperatures close to those at which it is to be applied. In the aging of the enamel slips, an equilibrium is set up between the clay, the frit, and the solution.

Preparation of Metal Parts.—The success of enameling depends on the nature and uniformity of the metal base to which the enamel is fused, and the obtaining of a parallelism between the coefficients of expansion of the enamel and the metal. The compositions of irons that can be enameled cover a wide range from commercially pure iron to high-carbon steels and cast irons, but no great variation can be tolerated for a given enameling process. A uniform grade of iron is very important. In the cast-iron enameling industry the castings are frequently made in the same factory in which they are enameled. The sheet-metal enameler usually purchases sheets to meet a definite specification. Before the liquid enamel (suspension in water) is applied to the metal, the surface must be thoroughly cleaned of all foreign matter, so that the enamel coating will adhere well to the metal and also not be affected itself. Cast iron is cleaned by pressure sandblasting. Occasionally the castings may also be annealed. Sheet metal is cleaned by pickling in 8 per cent sulfuric acid at 140°F. after the iron has been annealed.

Application of the Enamel.—Enamel may be applied to the metal in a number of different ways. Sheet-iron coats are generally applied by dipping or slushing, since the ware is usually coated on all sides. Slushing differs from draining in that the enamel slip is thicker and must be shaken from the ware. It is convenient for small odd-shaped pieces. A third method of application is spraying. Any of these three processes may be employed wet or dry. Cast-iron treatment is very similar to that for sheet iron, but slushing here consists of pouring the enamel slip over the casting and allowing the excess to run off. The enamel is now air-dried, and colors are brushed and stenciled on if wanted. Sometimes the enamel is applied in two coats.

Firing.—All enamels should be fired on the ware to melt them into a smooth, continuous, glassy layer. The requirements for successful firing of a good enamel are (1) proper firing temperature, 1400 to 1600°F., (2) time, 1 to 15 min., (3) [illegible]port of the ware, (4) uniform heating and cooling of the ware, [illegible] atmosphere free from dust. Heat is provided in either intermittent-fired muff[illegible] continuous tunnel furnaces. The product is taken from the fu[illegible] given many tests for its thermal, optical, physical, and chemical properties. The ware is now ready for use. The special enamel- or glass-lined equipment so extensively used in chemical plants is tested even by high-frequency waves to exclude any defects which only this method will detect but which in course of use would offer an avenue for acid penetration.

KILNS

The vitrification of ceramic products and the prior unit processes of dehydration, oxidation, and calcination are carried out in kilns that may be operated in a periodic or continuous manner. Muffle kilns are also used. Almost any type of kiln may be used for firing. Among the most used types are open-flame kilns where the ware is exposed to direct flame, kilns in which the ware is placed in saggers to keep it clean and to temper the heating, muffle kilns in which the flame is around a ceramic muffle, continuous kilns which at present are usually tunnels. Coal, gas, oil, or electricity may be used for fuel. The choice of the kiln and fuel[1] is largely a question of economics and the quality desired in the finished product.

Downdraft Kilns.—Downdraft periodic or batch kilns are the most common type. They are used in burning face brick, sewer pipe, stoneware, tile, and common brick. They may be either round or rectangular in shape. In them the heat is raised from room temperature to the finishing temperature for each burning operation. The kiln is "set" (filled with wares to be burned) and the heating started. The temperature is raised at a definite rate until the firing temperature is reached. The downdraft kiln is so named because the products of combustion go down in passing over the ware set in the kiln. The gases leaving the furnace go up inside the walls to the crown of the kiln and are pulled through the ware by means of a system of flues connected to an outside stack.

Updraft Kilns.—The updraft kiln has been most commonly used in burning pottery ware but is rapidly being replaced by tunnel kilns. It is similar to the downdraft type except for the movement of the gases. It gives better heat control than does the downdraft type.

Tunnel Kilns.—This kiln is a continuous one and consists of a long insulated tunnel through which the ware is passed continuously on loaded cars. The cars are moved usually at the rate of from 3 to 8 ft. per hr. and are in the kiln from 50 to 100 hr. Conditions in a given section of the tunnel are constant at all times. This is the best kiln for large installations burning volume products. It is not so well adapted to small batches of variable products that need changed conditions of time and temperature for best firing.

Continuous Chamber Kilns.—This kiln consists of a succession of chambers connected by means of flues or a long tunnel. It has been used more in Europe than in America. The heat from one chamber is passed to another countercurrent to the ware. *Because the chambers are burned in succession, the operation is continuous. There is always* one chamber cooling, another chamber being fired, and another chamber being heated by the waste of the two other chambers.

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[1] NORTON, *op. cit.*, p. 355, tabulates fuel consumption for periodic and tunnel kilns.

Clamp Kilns.—The clamp kiln is used in burning common brick and is temporary in nature. It is of the updraft type and has no flue system or top. It consists of side walls with spaces for arches to be used in burning.

Scove Kilns.—Most common brick are burned in scove kilns, which are really variations on the updraft type of furnace. The kiln itself is built from the green brick and is covered with a layer of burned brick. After burning, the kiln is completely dismantled. Because of this there is no possibility of permanent control devices.

Muffle Furnaces.—Kilns in which the products of combustion are not allowed to come in contact with the material being burned are called *muffle* kilns. Terra cotta is an example of a material fired in muffle kilns.

Problems

1. A pottery kiln is made up of a 4-in. layer of firebrick and an 8-in. layer of building brick, the latter being on the outside where the temperature is 125°F. The temperature within the kiln is 2500°F. The thermal conductivities for firebrick and brick are 0.62 and 0.42 B.t.u. per hr.-ft.^{2} per °F. per ft., respectively. Assuming perfect contact between the layers, calculate,

a. The rate of heat flow through the wall B.t.u. per hr.-ft.^{2}

b. The temperature at the junction of the two layers.

2. A test run is being made on a tunnel kiln used for firing bricks. The kiln is coal-fired, and all ash is removed by allowing it to drop into a pit filled with water. Evaporated water enters the stack with other gases. The tunnel holds 36 cars. One car is removed every 2 hr. and each car carries 900 bricks. Calculate the amount of heat and percentage loss due to

a. Sensible heat in dry flue gas.

b. Sensible heat in refuse.

c. Heat carried out by clay and clay structure of the kiln.

d. Unburned CO in flue gas.

e. Heat loss due to C in refuse.

Use the following data:

Analysis of Coal:

	Per Cent
H_2	5.22
C	76.17
N_2	1 50
O_2	7.65
S	1 92
Ash	7.54
Calorific value	13,830 B.t.u. per lb.
Total coal fired	1,937 lb.

Analysis of Refuse:

	Per Cent
H_2O	0.15
Volatile	1.65
Fixed C	28.66
Ash	69.54

Temperatures:

Atmosphere	79°F.
Flue gas	340°F.

Specific Heat (at 209.5°F.):

	B.t.u. per lb.°F.
Clay	0.23
CO_2	0.2095
O_2	0.2167
N_2, CO	0.2471
Steam	0.491 (between 212° and 340°)

(Latent heat of vaporization of water = 967 B.t.u. per lb.)

Ashpit holds 566 lb. H_2O.

4.735 lb. wet ash as removed weighed 2.71 lb. after drying.

Boiling point H_2O = 212°F.

Flue Gas Analysis:

	Per Cent
CO_2	3.29
CO	0.16
N_2	79.88
O_2	16.67

Removable percentage of water in bricks = 4.55.

Green ware = 17,100 lb.

Clay structure in kiln = 7,100 lb.

Assume heat content of all other parts of structure as negligible, heat content of moisture as a product of combustion and is driven out of the clay ware as negligible.

The cars containing the clay came out at a temperature of 900°F.

Heat of combustion of CO = 4,380 B.t.u. per lb.

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CHAPTER XI

CEMENTS, CALCIUM AND MAGNESIUM COMPOUNDS

The industrial uses of limestone and cements have provided important undertakings for chemists and engineers since the early years when lime mortars and natural cements were introduced. In modern times one needs only mention reinforced-concrete walls and girders, tunnels, dams, and roads to realize the dependence of present-day civilization upon these products. The convenience, cheapness, adaptability, strength, and durability of both lime mortar and cement products have been the foundation of these tremendous applications. The once crude and intermittent type of production has been perfected to a point where 6,000,000 tons of lime and over 225,000,000 barrels of cement were produced in the United States in 1942 (Table 1).

CEMENT

In spite of our modern concrete roads and buildings everywhere around us, it is difficult to realize the tremendous growth of the cement[1] industry during the past century. Man had early discovered certain natural rocks which through simple calcination gave a product that hardened on the addition of water. Yet the real advance did not take place until chemical analysis and chemical engineering laid the basis for the modern efficient plants working under closely controlled conditions on a variety of raw materials.

Historical.—In 1824 an Englishman, Joseph Aspdin, patented an artificial cement which he called *portland* because concrete made from it resembled a famous building stone obtained from the Isle of Portland near England. Very shortly, off the coast of Harwick, as many as 300 boats were engaged in dredging for "cement stones." These were argillaceous limestone which, upon being burned, would harden when water was added and not fall to a powder as would ordinary limestone.[2] Cement so made, irrespective of brand, is known as *portland cement* to distinguish it from natural or pozzuolana and other cements.

Uses and Economics.—A generation ago concrete was little used in this country because the manufacture of portland cement was a

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[1] BOGUE, Portland Cement and the "Plastic" Concrete, *Paper* 41, Portland Cement Association Fellowship of the National Bureau of Standards, 1942. This is an excellent general summary.

[2] WATSON, Discovery of Roman Cement, *Rocks and Minerals*, **15**, 272 (1940).

complicated expensive process. Thanks to the invention of laborsaving machinery, cement is now low in cost and is applied everywhere in the construction of homes, public buildings, roads, industrial plants, dams, bridges, and in many other places. Table 1 indicates the large volume of this industry.

CEMENT MANUFACTURE

It would be well at the outset to define various types of cements:

1. *Pozzuolana Cement.*—Since the beginning of the Christian era the Italians have successfully employed pozzuolana cement, made by grinding two to four parts of a pozzuolana with one part of hydrated lime. A pozzuolana is a material which is not cementitious in itself but which becomes so upon admixture with lime. The natural pozzuolanas are volcanic tuffs and the artificial ones are burnt clays and shales.[1]

2. "*Portland cement* is the product obtained by finely pulverizing clinker made by calcining to incipient fusion an intimate and properly proportioned mixture of argillaceous and calcareous materials, with no additions subsequent to calcination excepting water and calcined or uncalcined gypsum." This is a flourlike powder which varies in color from a greenish gray to a brownish gray.

Portland cement may be subdivided into four classes:[2] *Regular* portland cements are the usual products required to meet no exacting or special demands. There is a white portland cement sold which contains less iron. Masonry cements are mixtures of cement with hydrated lime, crushed limestone, diatomaceous earth, with or without small additions of calcium stearate, petroleum, or highly colloidal clays. These are easily workable because of increased plasticity. *High-early-strength* (H.E.S.) cements are made from a raw material with a high lime to silica ratio, frequently burned twice, and very finely ground. They contain a higher proportion of tricalcium silicate, C_3S, than regular portland cements and hence harden much more quickly and with greater evolution of heat. Roads constructed from H.E.S. cement can be put into service more quickly than if regular cement had been employed. *Low-heat* portland cements contain a higher percentage of tetracalcium aluminoferrite, C_4AF, and dicalcium silicate, C_2S, and hence set with the evolution of much less heat, as can be seen from the data given in Table 5. Also the tricalcium silicate, C_3S, and the tricalcium aluminate, C_3A,

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[1] LEA and DESCH, "Chemistry of Cement and Concrete," pp. 244–267, Longmans, Green and Company, New York, 1935.

[2] BATES, How Many Cements Needed? *Rock Products*, **38**, 51–53 (August, 1939). Specifications are given for these various types of cement in Federal Standard Stock Catalog, Sec. IV (Part 5). Federal Specification SS-C-191a, Cement; Portland; SS-C-206, Cement; Portland, Moderate-heat-of-hardening; SS-C-201, Cement; Portland, High-early-strength; SS-C-211, Cement; Portland, Sulfate-resisting—all 1936.

are lower. Actually the heat evolved should not exceed 60 and 70 cal. per gram after 7 and 28 days, respectively, and is 15 to 35 per cent less than the heat of hydration of regular or H.E.S. cements. There are also available *chemical-* or *sulfate-resisting* portland cements which by their composition or processing resist chemicals better than the other three types. These cements are higher in tetracalcium aluminoferrite, C_4AF, and lower in tricalcium aluminate, C_3A, than the regular cements. Additions during grinding of small percentages of calcium stearate or sodium silicate are somewhat effective. There is, however, no such thing as an acidproof portland cement.

3. *High-alumina cement* is manufactured by fusing a mixture of limestone and bauxite, the latter usually containing iron oxide, silica, magnesia, and other impurities. It is characterized by a very rapid rate of development of strength and superior resistance to sea water and sulfate-bearing water.

4. *Special* or *acid-resisting cements* are on the market and find use in erecting acid washing towers and for mortar in laying floors or walls to resist acids. A high-silica water glass mixed into a dough with silica sand or coarse asbestos powder has found favor. This is frequently "set" with a strong sulfuric acid wash. Likewise molten sulfur containing some filler such as asbestos, or sand is poured into brick joints.[1]

TABLE 1.—CEMENT SHIPMENTS IN 1942[a]

Variety	No. of plants	Barrels	Value per barrel	Total value
Portland	155	185,300,884	$1.53	$283,257,028
H.E.S. portland	87	7,065,700	1.94	13,683,665
Masonry mixtures	48	2,079,015	1.50	3,115,799
Low-heat portland	60	13,404,761	1.43	19,136,773
Portland-pozzuolana	7	329,637	1.41	465,627
White portland	5	306,120	3.97	1,214,442
Art-well portland	17	552,157	1.99	1,100,296
Sulfate-resisting portland	8	77,015	1.78	136,939
Miscellaneous	12	269,705	1.74	468,083
Pozzuolana	11	2,508,324	1.46	3,668,169
Total	...	211,893,318	.....	$326,246,821

[a] Mineral Industry Surveys, M.M.S. 1103, 1104, 1105, U.S. Bureau of Mines, 1943. A barrel of cement weighs 376 lb. and is equivalent to four sacks.

Raw Materials.—Portland cement is made by mixing and calcining calcareous and argillaceous materials in the proper ratios. Table 2 summarizes the raw materials consumed. Formerly a large proportion of cement was burned from an argillaceous limestone known as *cement*

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[1] PERRY, *op. cit.*, pp. 944–945; GREENWOOD and SNELLING, Some Lutes and Cements, *Chemistry & Industry*, **56**, 1152–1154 (1937).

rock which is found in the Lehigh district of Pennsylvania and New Jersey. This material was first used as a natural cement but, when found deficient in lime, was corrected by adding a small proportion of limestone. In addition to the natural materials some plants use artificial products such as blast-furnace slag and precipitated calcium carbonate obtained as a by-product in the alkali and synthetic ammonium sulfate industry. Sand, waste bauxite, and iron ore are sometimes consumed in small amounts to adjust the composition of the mix. Gypsum (2 to 3 per cent) is added to prevent too rapid setting of the tricalcium aluminate.

Cement Rock Beneficiation.—Froth flotation, or beneficiation[1] is now the principal step in a process for obtaining cement kiln charges of correct chemical and physical composition, for all types of cement manufacture, from available raw materials which may be either inferior or actually unusable as quarried. The trend in cement composition has been toward higher silica, lower alumina, less alkali, and more iron.

TABLE 2.—RAW MATERIALS FOR CEMENT[a]

	Tons
Limestone and cement rock	24,290,000
Clay and shale	2,400,000
Blast-furnace slag	600,000
Marl	660,000
Uncalcined gypsum	460,000
Oyster shells	700,000

[a] Statistical Abstract of the United States, 1939.

Chemically these specification changes result in a cement with slower setting time, less heat of hydration, more resistance to alkaline earths and waters. In a physical way these new specifications have demanded a more thorough control of the actual mechanical operation of the cement plant itself. Clinker has to be burned at constant temperatures using pyrometers to indicate the condition in the kilns; finer grinding is necessary to give better strengths at earlier dates to offset the retarding of the setting time due to the change in specifications. All of these changes have been in the direction of improving the endurance of the concrete.[2]

The complete beneficiation process involves a combination of grinding, classification, flotation, and thickening operations, each ~~adapted to~~

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[1] ENGELHART, Flotation as Applied to Modern Cement Manufacture, *Ind. Eng Chem.*, **32**, 645 (1940). This article includes a detailed flow sheet for the Brierwood process used at the plant of the Valley Forge Cement Co., together with patents and other references. At Valley Forge there are a coarse and a fine lime flotation circuit, together with two silicate flotation circuits. Nine plants are now operating and a large one building using these procedures of the Separation Process Company. For an excellent short summary of flotation, including agents, equipment, and many references, see Perry, *op. cit.*, pp. 1732–1740.

[2] DOUGLASS, Separation Process Company, Catasauqua, Pa., *private communication.*

satisfy the specific requirements of the cement desired and the peculiar characteristics of the individual raw materials. The purpose is to "beneficiate" available materials; *i.e.*, to correct the proportions of the mineral sources of the four oxides of calcium, silicon, aluminum, and iron, essential for cement manufacturing, and discard useless constituents. This may involve the raising of the lime content of the raw material as at Valley Forge, or it may call for the elimination of the greater part of the silica as compared to the alumina. To do this requires flexibility in the processing and the choice of varying reagents which in one plant will float off one mineral and which at a different plant will remove another constituent.

The raw materials are usually ground very finely to free the mineral constituents and then put through a hydroseparator, as shown in Fig. 1.

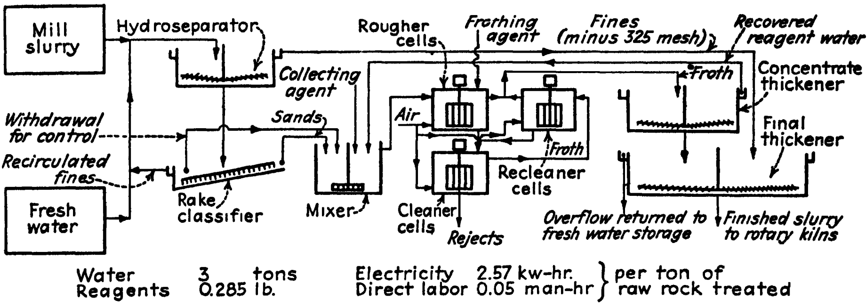

FIG. 1.—Cement rock beneficiation.

Here the hydrooverflow is not processed, going directly to the final thickener. With some other minerals the hydrooverflow would need to have some constituent removed by flotation. But in Fig. 1 the hydrounderflow, after further size classification, has the sands or coarser particles subjected to flotation to remove calcite and reject mica and talc.

The success of the process in making these differential separations is attributed principally to the use of very small quantities of collecting reagents added in small increments to the pulp in each cell in a stage-oiling circuit. The collecting agent must selectively wet or "film" the mineral to be removed and act with the air to cause the particles to be lifted to the surface, there to be caught in the froth and removed. In Fig. 1, oleic acid may be employed as the collector in the concentration of 0.5 lb. per ton of feed. The typical frothers are satisfactory (monohydric long-chain alcohols, dilute resinates, and cresylic acid). A concentration of .04 lb. per ton of rock suspended in 4 tons of water has given good results. Frothing aids in the separation. As is shown in Fig. 1, the concentrate thickener returns to the circuit, the recovered reagent water.

Unit Operations, Unit Processes, Energy Requirements.—Essentially the unit operations prepare the raw materials in the necessary proportions and in the proper physical state of fineness and intimate contact so that the chemical reactions (unit processes) can take place at the calcining temperature in the kiln to form, by double decomposition or neutralization, the following compounds:

Formula	Name	Abbreviation
$2CaO \cdot SiO_2$	Dicalcium silicate	C_2S
$3CaO \cdot SiO_2$	Tricalcium silicate	C_3S
$3CaO \cdot Al_2O_3$	Tricalcium aluminate	C_3A
$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	Tetracalcium aluminoferrite	C_4AF
MgO	In free state	

K_2O and Na_2O form small amounts of various compounds with CaO, Al_2O_3, SiO_2, and SO_3.

Other reactions take place, such as dehydration of clay and decarbonization of limestone, these both being endothermic, with values of about 380 and 665 B.t.u. per lb., respectively. The clinker formation is exothermic with a probable value of 200 B.t.u. per lb. of clinker.[1] Probably the net heat requirements are in the neighborhood of 900 B.t.u. per lb. of clinker. However, the coal consumption indicates an expenditure of 3,000 or 4,000 B.t.u. per lb. of clinker.[2] This heat is evolved in the kiln in carrying out the following reactions, as tabulated by Lea and Desch:

Temperature	Reaction	Heat change
100°C.	Evaporation of free water	Endothermic
500°C. and above.	Evolution of combined water from clay	Endothermic
900°C. and above. .	Evolution of carbon dioxide from calcium carbonate	Endothermic
900–1200°C.	Main reaction between lime and clay	Exothermic
1250–1280°C.	Commencement of liquid formation	Endothermic
1280°C. and up. . . .	Further formation of liquid and compounds	Probably endothermic

It should be noted that most of the reactions in the kiln proceed in the solid phase, and that only toward the end is a melt formed. All these reactions are embraced in the "burning of cement."[3]

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[1] LEA and DESCH, *op. cit.*, p. 105.

[2] *Cf.* LACEY and WOODS, Heat and Material Balances for a Rotary Cement Kiln, *Ind. Eng. Chem.*, **27**, 379 (1935).

[3] MARTIN, "Chemical Engineering and Thermodynamics Applied to the Cement Rotary Kiln," The Technical Press, Ltd., London, 1932. This book is filled with

Manufacturing Procedures.—Two methods of manufacture are used: the wet and the dry processes. The *wet process*, though the original one, was displaced for a time by the dry process but is now being adopted largely for new plants because of the more accurate control and mixing of the raw mixture which it affords. This is illustrated in the generalized flow sheet[1] of Fig. 2. The solid material after dry crushing is reduced to a fine state of division[2] in wet tube or ball mills and passes as a slurry through bowl classifiers or screens. The slurry is pumped to correcting tanks where rotating arms make the mixture homogeneous and allow the final adjustment in composition to be made. This slurry is filtered in a continuous rotary filter and fed into the kiln. The *dry process* is especially applicable to hard materials. In this process the materials are roughly crushed in jaw crushers followed by gyratory mills, then dried, sized, and more finely ground in tube mills (see Fig. 3). This dry, powdered material is fed directly to the rotary kilns where the previously mentioned chemical reactions take place. Heat is provided by burning oil, gas, or pulverized coal, using preheated air from cooling the clinker.

The tendency in recent years has been to lengthen the rotary kiln in order to increase its thermal efficiency. Dry process kilns may be as short as 150 ft., but in the wet process, 300- and 400-ft. kilns are not uncommon. The internal diameter is usually from 9 to 11 ft. The kilns are rotated at from ½ to 2 r.p.m., depending on size. The kilns are slightly inclined so that materials fed in at the upper end travel slowly to the lower and firing end, taking from 2 to 3 hr.

In order to obtain greater heat economy, processes are used for removing part of the water from the slurry. Some of the methods used are slurry filters (as Fig. 2 shows) and Dorr thickeners. Some other common adjuncts to rotary kilns are cyclone dust separators and Cottrell precipitators. Waste-heat boilers are sometimes used to conserve heat and are particularly saving on dry-process cement where the waste gases from the kiln are hotter than from the wet process and may reach 800°C.

Because of the fact that the lining of the kiln has to withstand severe abrasions and chemical attack at the high temperatures in the clinkering zone, the choice of a refractory lining is difficult. For this reason high-alumina bricks are widely used, although portland cement clinker itself is satisfactory.

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data and calculations pertaining to cement. Chapter 9 considers the heat absorbed n making clinker. Chapter 15 presents the concept of entropy in burning cement as "high-grade heat" or heat at the right thermal pressure or temperature.

[1] A pictured flow sheet with details of grinding and other equipment, is given in *Chem. & Met. Eng.*, **46**, 629 (1939). This is a description of the wet process of the Lone Star Cement Co., Hudson, N.Y.

[2] PERRY, *op. cit.*, pp. 1956–1957, 1612–1614, presents some details on this matter.

The final product formed consists of hard granular masses from ⅛ to ¾ in. in size called *clinker*. The clinker falls through openings in the stationary firing ring of the kiln into rotating coolers which simultaneously preheat the combustion air. Pulverizing followed by fine grinding in tube or ball mills and automatic packaging complete the steps to the finished cement. The clinker is ground dry by various hookups. Figure 3 illustrates some of these arrangements. However, Perry[1] presents more details of actual grinding circuits with power requirements.

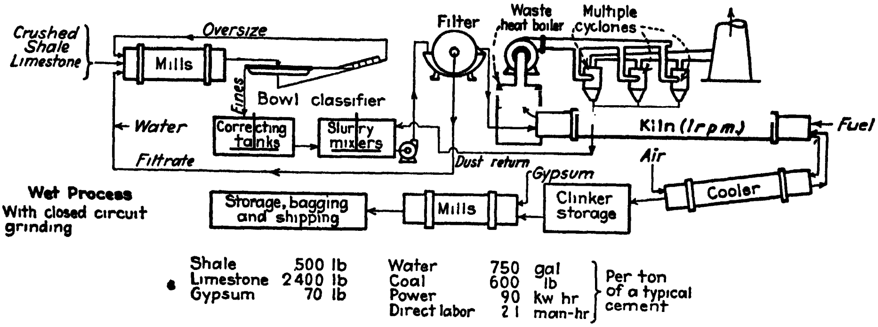
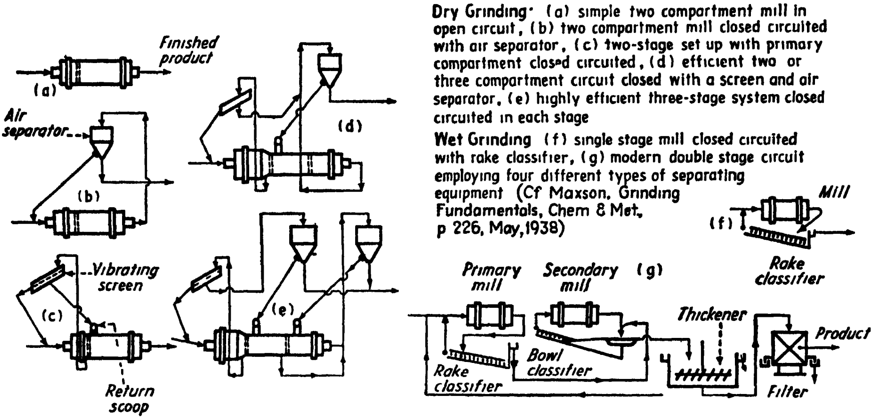


Fig. 2.—The manufacture of portland cement.



Dry Grinding: (a) simple two compartment mill in open circuit, (b) two compartment mill closed circuited with air separator, (c) two-stage set up with primary compartment closed circuited, (d) efficient two or three compartment circuit closed with a screen and air separator, (e) highly efficient three-stage system closed circuited in each stage

Wet Grinding (f) single stage mill closed circuited with rake classifier, (g) modern double stage circuit employing four different types of separating equipment (Cf Maxson, Grinding Fundamentals, Chem & Met, p 226, May, 1938)

Fig. 3.—Dry and wet grinding hookups.

Compounds in Cement.—In portland cements we have a mixture of compounds (previously listed) present in amounts partly dependent on the degree of attainment of equilibrium conditions during burning. Tables 3 and 4 give analyses of various types of portland cement and an average composition of some 102 regular cements. From these analyses it is seen that portland cement composition lies in a rough approximation in the system $CaO\text{-}SiO_2$, in a closer approximation in the system $CaO\text{-}SiO_2\text{-}Al_2O_3$, and to a still closer approximation in the five-component system $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Fe_2O_3\text{-}MgO$. A complete understanding of portland cement would require a knowledge of the phase equilibrium relations of the high-lime portions of all the two-, three-, four-, and five-component systems involved. Of these, all 10 of the two-component systems are known, most of the 10 three-component systems, and those parts of the four-component systems, $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Fe_2O_3$ and $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}MgO$, in which portland cement compositions are located.[1] Modern cement technology is largely based on the system $CaO\text{-}Al_2O_3\text{-}SiO_2$ which was worked out by Rankin and Wright[2] at the Geophysical Laboratory.

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[1] *Ibid.*, tube and ball mills, pp. 1904, 1957–1960, 1907, roller mills, pp. 1927–1931. The entire Sec. 16 of Perry should be carefully studied in this connection.

TABLE 3.—ANALYSES OF PORTLAND CEMENTS
(In percentage)

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Alkali	SO_3
	Regular cement (average of 102)						
Minimum.....	61.17	18.58	3.86	1.53	0.60	0.66	0.82
Maximum....	66.92	23.26	7.44	6.18	5.24	2.9	2.26
Average......	63.85	21.08	5.79	2.86	2.47	1.4	1.73
	High-early-strength (average of 8): high C_3S						
Minimum.....	62.7	18.0	4.1	1.7	....	....	2.2
Maximum....	67.5	22.9	7.5	4.2	....	....	2.7
Average......	64.6	19.9	6.0	2.6	....	....	2.3
	Low-heat-of-setting (average of 5): high C_4AF and C_2S, low C_3S and C_3A						
Minimum.....	59.3	21.9	3.3	1.9	....	....	1.6
Maximum....	61.5	26.4	5.4	5.7	....	....	1.9
Average......	60.2	23.8	4.9	4.9	....	....	1.7

TABLE 4.—PERCENTAGE COMPOSITION OF 102 REGULAR PORTLAND CEMENTS IN TERMS OF COMPOUNDS. CALCULATED FROM TABLE 3

	C_3S SiO_2	C_2S CaO	C_3A Al_2O_3	CaO Al_2O_3. C_4AF Fe_2O_3.	$CaSO_4$ SO_3.	MgO
Minimum................	35.3	0	0	4.7	1.4	0.60
Maximum................	70.6	33.2	15.5	18.4	3.8	5.24
Average..................	51.7	21.4	10.5	8.7	2.9	2.47

NOTE: These compound compositions are computed from the oxide analysis as follows: (1) Put all SO_3 in $CaSO_4$, (2) put all Fe_2O_3 in C_4AF, (3) put remaining Al_2O_3 in C_3A, (4) divide remaining CaO and SiO_2 stoichiometrically between C_2S and C_3S, (5) assume MgO is in free state and neglect Na_2O and K_2O.

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[1] LEA and DESCH, *op. cit.* Chapter IV treats of phase relations.

[2] RANKIN and WRIGHT, The Ternary System: $CaO\text{-}Al_2O_3\text{-}SiO_2$, *Am. J. Sci.*, **39**, 1–79 (1915).

It can be observed for the regular cement compositions presented in Tables 3 and 4 that a change of CaO percentage from 61.17 to 66.92 alters the C_3S percentage from 35.3 to 70.6 and the C_2S from 0 to 33.2.

Setting or Hardening of Cement.—Although many theories have been proposed to explain the setting or hardening of cement, it is generally agreed that this takes place by *hydration* and *hydrolysis*.[1] The following equations represent these reactions:

$CaO + xH_2O \rightarrow CaO \cdot xH_2O$

$$C_2S + xH_2O \rightarrow C_2S \cdot xH_2O \text{ (amorph.)}$$

$$C_3S + xH_2O \rightarrow C_2S \cdot xH_2O \text{ (amorph.)} + Ca(OH)_2 \text{ (crystal.)}$$

$SiO_2 + H_2O \rightarrow SiO_2 \cdot xH_2O$

Al_2O_3

$$C_3A + 6H_2O \rightarrow C_3A \cdot 6H_2O \text{ (crystal.)}$$

$$C_3A + 3(CaSO_4 \cdot 2H_2O) + 25H_2O \rightarrow C_3A \cdot 3CaSO_4 \cdot 31H_2O$$

$$C_4AF + xH_2O \rightarrow C_3A \cdot 6H_2O \text{ (crystal.)} + CaO \cdot Fe_2O_3 \cdot (x - 6)H_2O$$

$$MgO + H_2O \rightarrow Mg(OH)_2$$

TABLE 5.—HEAT OF HYDRATION[a]
(Calories per gram)

Compound	Days				
	3	7	28	90	180
C_4AF	29	43	48	47	73
C_3A	170	188	202	188	218
C_2S	19.5	18.1	43.6	55.2	52.6
C_3S	98.3	110	114.2	122.4	120.6

[a] ROBERTSON, Boulder Dam, *Ind. Eng. Chem.*, **27**, 242 (1935).

The hydration products have very low solubility in water. If this were not true, concrete would be rapidly attacked in contact with water.

In recent years much attention has been given to the heat evolved during the hydration of cement. The various compounds contribute to the heat of setting as follows:

$$C_3A > C_3S > C_4AF > C_2S^2$$

Table 5 shows why low-heat-of-setting cements are made low in C_3A and

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[1] SLIEPCEVICH, GILDART, and KATZ, Crystals from Portland Cement Hydration, *Ind. Eng. Chem.*, **35**, 1178 (1943).

[2] WOODS, STEINOUR, and STARKE, Effect of Composition of Portland Cement on Heat Evolved during Hardening, *Ind. Eng. Chem.*, **24**, 1212 (1932). *Cf.* ROGUE and LERCH, Hydration of Portland Cement Compounds, *Paper* 27, Portland Cement Association Fellowship at National Bureau of Standards, Washington, 1934.

C_3S but high in C_2S. This is accomplished (1) by adding more Fe_2O_3 which takes the Al_2O_3 out of circulation as C_4AF, thereby diminishing the amount of C_3A and (2) by decreasing the CaO/SiO_2 ratio. Notice these facts in the analyses in Table 3. This low-heat-of-setting cement was used in the construction of Boulder Dam to avoid cracking the structure from heat stresses during setting and cooling As an additional safeguard the structure was cooled during setting by circulating cold water through 300 miles of lightweight 1-in pipe placed in the concrete mass [1]

TABLE 6 —STRENGTH CONTRIBUTION OF VARIOUS COMPOUNDS[a]
(Strength of briquettes of pure compounds)

1 day	$C_3A > C_3S > C_4AF > C_2S$
3 days	$C_3A > C_3S > C_4AF > C_2S$
7 days	$C_3A > C_3S > C_4AF > C_2S$
28 days	$C_3A > C_3S > C_4AF = C_2S$
3 months	$C_2S > C_3S = C_3A = C_4AF$
1 year	$C_2S > C_3S > C_3A = C_4AF$
2 years	$C_2S > C_3S > C_4AF > C_3A$

NOTE $C_2S\,xH_2O$ (amorph), whose structure and nature are unknown is the principal source of strength of the set cement

[a] *Cf* GONNERMAN, Study of Cement Compositions *Proc Am Soc Testing Materials* **34**, 244 (1934).

Tables 6 and 7 present further facts regarding the functions of the different compounds in the setting of cement. To hold up the "flash set" caused by C_3A, some investigators assert that the gypsum added as a retarder[2] causes the temporary formation of $C_3A\,3CaSO_4{\cdot}31H_2O$, while others believe that the gypsum gives free $Ca(OH)_2$ by reaction with alkali, and this in turn forms the more stable tetracalcium aluminate, $4CaO\,Al_2O_3$

TABLE 7 —FUNCTION OF COMPOUNDS

Compound	Function
C_3A	Responsible for initial set (flash set)
C_3S	Responsible for first strength (at 7 or 8 days)
C_2S and C_3S	Responsible for final strength (at 1 year)
Fe_2O_3, Al_2O_3, Mg, and alkalies	Lower clinkering temperature

SPECIAL CEMENTS

For acid conditions, portland cement is unsuitable as the cementitious constituents are dissolved. For these extreme conditions, special cements have been developed, of which two types have received industrial acceptance. The older type is based upon finely divided silica which is mixed just before using with a high-silica (Na_2O to SiO_2 = 1 to 3.25) water glass of 38°Bé. Some of these sodium silicate cements are hardened by being given a strong sulfuric acid wash, but others[1] harden of themselves. In recent years, apparatus as well as cements has been constructed of phenol-formaldehyde resins as the binding material with an inert filler such as carbon or acid-washed asbestos fiber.

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[1] ROBERTSON, Boulder Dam., *Ind. Eng. Chem.*, **27**, 242 (1935).

[2] LEA and DESCH, *op. cit.*, pp. 191–194.

LIME

Historical.—Although lime has been employed as a building material for centuries, very little exact information about its properties has been available until recently. Although the manufacture of lime and its use can be traced back throughout Roman, Greek, and Egyptian civilizations, the first definite written information concerning lime was handed down from the Romans. In his book, "De Architectura," Marcus Pollio, a celebrated engineer and architect who lived during the reign of Augustus (27 B.C. to A.D. 14), deals quite thoroughly with the use of lime for mortar involved in the construction of harbor works, pavements, and buildings.

In the early days of the young American colony, the crude burning of limestone was one of the initial manufacturing processes engaged in by the settlers, using "dug-out" kilns built of ordinary brick or masonry in the side of a hill, with a coal or wood fire at the bottom and a firing time of 72 hr. These can still be seen in many of the older sections of the country. It was not until recent years that, under the influence of scientific cooperative research, the manufacture of lime has developed into a large industry under exact technical control, with the resulting uniformity of products.

Uses and Economics.—Lime itself may be used for medicinal purposes, insecticides, plant and animal food, gas absorption, precipitation, dehydration, and causticizing. It is employed as a reagent in the sulfite process for papermaking, dehairing hides, recovering by-product ammonia, manufacturing of high-grade steel and cement, water softening, manufacturing of soap, rubber, varnish, and refractories, and the making of sand-lime brick. Lime is indispensable for mortar and plaster use and serves as a basic raw material for calcium salts and for improving the quality of certain soils. Figure 4 summarizes the main statistics.[2] However, under the stimulus of the Second World War, the total lime sold or used by producers reached 6,076,000 tons for 1942.

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[1] The Pennsylvania Salt Manufacturing Company of Philadelphia has been specializing in acidproof cements (their Penchlor acidproof cement is resistant to most acids). This company also makes a resin cement (Asplit) which is composed of a solution of a self-hardening phenol-formaldehyde resin which is to be mixed with an acidproof powder just before use. The acidproof powder frequently consists of carbon. Such cements are quite resistant to acids. All of these are attacked by alkali.

[2] *Cf.* WING, Lime as a Chemical Raw Material, *Chem. Industries*, **50**, 612–617, 760 (1942).

Lime is sold as a high-calcium quicklime containing not less than 90 per cent of calcium oxide and from 0 to 5 per cent of magnesia with small percentages of calcium carbonate, silica, alumina, and ferric oxide present as impurities. The suitability of lime for any particular use depends on its composition and physical properties, all of which can be controlled by the selection of the limestone and the detail of the manufacturing process. Much lime must be finely ground before use.[1]

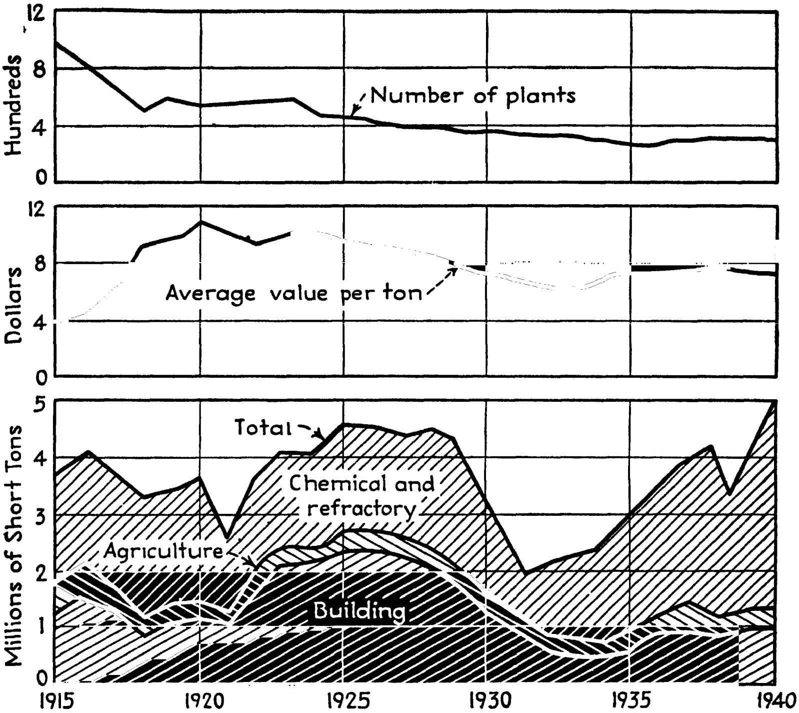

FIG. 4.—Trends in number of active lime plants, average value per ton, and principal uses, 1915–1940. (*From Bureau of Mines Minerals Yearbook Review of* 1940.)

Depending on composition, there are several distinct types of limes. Hydraulic limes are obtained from the burning of limestone containing clay, and the nature of the product obtained after contact with water varies from a putty to a set cement. The high-calcium-content limes harden only by absorption of carbon dioxide from the air, which is a slow process; hydraulic limes also harden slowly but they can be used under water. For chemical purposes high-calcium lime is required except for the sulfite paper process where a magnesian lime works better.

Although in many sections of the country the high-calcium lime is preferred by the building industry for the manufacture of its mortar or its lime plaster, there are places where limestone containing some magnesium is burned or where even a dolomitic stone is calcined. Typical compositions of such stones are given in Table 8. These products, called *magnesian* limes or *dolomitic* limes,[1] find favor in the hands of some plasterers who claim they work better under the trowel. In the metallurgical field, "refractory lime" as dead-burned dolomite or as raw dolomite is employed as a refractory patching material in open-hearth furnaces, being applied between heats to repair scored and washed spots in the bottom of the furnace.

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[1] PERRY, *op. cit.*, pp. 1954, 1960.

Hydrated lime is finding increased favor in the chemical and building trades over the less stable quicklime, despite its increased weight. The quicklime is almost invariably slaked or hydrated before use.

TABLE 8.—APPROXIMATE COMPOSITION OF DOLOMITIC LIMESTONES[a]

Constituent	Per Cent
CO_2	30–45
SiO_2	1–5
Fe_2O_3	0–2
Al_2O_3	0–5
CaO	35–45
MgO	10–25
$Na_2O + K_2O$	0–3

NOTE: All components are expressed as the oxides.

[a] PIERCE and HAENISCH, "Quantitative Analysis," p. 300, John Wiley & Sons, Inc., New York, 1937.

Because of the better slaking and the opportunity to remove impurities, factory hydrate[2] is purer and more uniform than the slaked lime prepared on the job.

LIME MANUFACTURE

Lime has always been a cheap commodity because limestone deposits are readily available in so many sections of the United States and hence permit its burning near centers of consumption.

Raw Materials.—The carbonates of calcium or magnesium are obtained from naturally occurring deposits of limestone, marble, chalk, or dolomite. For chemical usage, a rather pure limestone is preferred as a starting material because of the high-calcium lime that results. The quarries furnish a rock that contains as impurities low percentages of silica, clay, or iron. Such impurities are important because the lime may react with the silica and alumina to give calcium silicates or calcium alumino-silicates which possess not undesirable hydraulic properties. The lumps sometimes found in "overburned" or "dead-burned" lime result from changes in the calcium oxide itself as well as from certain impurities acted upon by excess heat, recognized as masses of relatively inert, semivitrified material. On the other hand, it often happens that rather pure limestone is calcined insufficiently, and lumps of calcium carbonate are left in the lime. This lime is spoken of as "underburned" lime.

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[1] To prevent "popping out," the MgO must be completely hydrated such as by steam hydration at 160°C. and under such pressure as 60 lb. per sq. in.

[2] PERRY, *op. cit.*, p. 1941, tabulates the results from grinding and air-separating hydrated lime from much of the impurities originally present in the quicklime wherein the purity is raised from 89 to 98 per cent, the tailing going to agricultural applications.

Energy Changes, Unit Operations, Unit Processes.—Energy is required for blasting out the limestone, for transporting and sizing it, for the burning or calcining process.[1] The reactions involved are for

Calcining:

$$CaCO_3 \rightleftarrows CaO + CO_2; \qquad \Delta H = +43{,}500 \text{ cal.}$$

Hydrating:

$$CaO + H_2O \rightarrow Ca(OH)_2; \qquad \Delta H = -15{,}900 \text{ cal.}$$

During the calcining the volume contracts and during the hydrating it swells. For calcination the average fuel ratios are, using bituminous coal: 3.23 lb. of lime from 1 lb. of coal in shaft kilns and 3.37 lb. in rotary kilns.[2] For high-calcium lime, a temperature of from 1000 to 1100°C. is usually carried.

The sequence of *unit operations* (Op.) and *unit processes* (Pr.) connected with manufacturing in such a kiln as shown in Fig. 5 are

Blasting down of limestone from quarry face, or occasionally from underground veins (Op.).

Transportation from quarry to mills, generally by industrial railroad (Op.).

Crushing and sizing of stone in jaw and gyratory crushers[3] (Op.).

Screening to remove various sizes (for example, a 4- to 8-in. stone implies that all pieces passing a 4-in. screen or retained on an 8-in. screen have been separated out) (Op.).

Carting of this large stone to top of vertical kilns (Op.).

Conveying of small rock to rotary kiln (Op.).

Conveying of fines to pulverizer to make powdered limestone for agricultural and other demands (Op.).

Burning of limestone according to size, in vertical kilns to give lump lime (Pr.), or horizontal rotary kilns to furnish fine lime (Pr.).

Packaging of finished lime in barrels (180 or 280 lb.) or sheet-iron drums (Op.), or conveying of lime to hydrator (Op.).

Hydration of lime (Pr.).

Packaging of slaked lime in 50-lb. paper bags.

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[1] *Ibid.*, pp. 744–746, presents the calculations for heat balance and gas analysis of a vertical lime kiln.

[2] MYER, Lime-fuel Ratios of Commercial Lime Plants in 1939, U.S. Bureau of Mines, *Ind. Circ.* 7174, 9 pp., 1941.

[3] PERRY, *op. cit.*, pp. 1890–1892.

Manufacturing Procedures.—For the burning of lump limestones, vertical kilns are almost universally employed (see Fig. 5). Their outside construction is sheet steel for strength and prevention of gas leakage, with a firebrick inner lining. In many cases the gases escape from the top, but in the ammonia soda industry the upright kilns are closed and under slight suction with pipes conducting the gases to compressors and thence to the carbonating towers. If the limestone is properly chosen and sized (4 to 8 in.), it passes through the kiln with the formation of a minimum amount of fines or overburned or underburned lime. Different-sized stones burn at different rates. These kilns are heated either by mixing the fuel in with the stone (in which case the ash contaminates the product) or by the use of coal grates or gas burners arranged along the outside of the kiln, as shown in Fig. 5. Such upright kilns operate continuously and produce up to 80 tons in 24 hr.

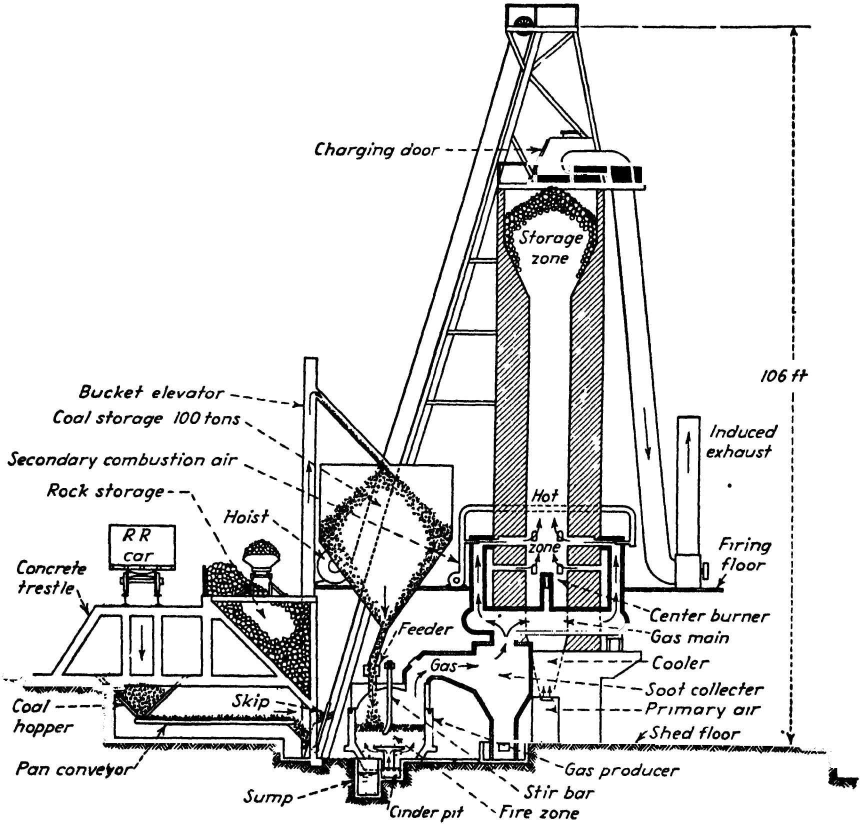

FIG. 5.—Gas-fired vertical lime kiln, producing 80 tons of high calcium lime per kiln per day. (*Victor J. Azbe, St. Louis, Missouri-patent granted.*)

In quarried limestone there is always a certain amount of stone that is so fine it would clog the upright kilns and prevent the passing of hot gases, causing uneven burning of the stone. This smaller limestone can be sold for metallurgical purposes or pulverized for agricultural use, or, after fines are screened out, it can be burned in rotary kilns. This latter procedure is becoming more common as the business of furnishing lime has been centralized in larger operations. These rotaries will calcine up to 200 tons of product in 24 hr., producing a fast slaking lime caused partly by the relatively short time of 3 hr. in the kiln. Marble, being crystalline and cleavable, breaks into smaller pieces and can be burned only in horizontal rotary kilns after being suitably sized. Precipitated calcium carbonate, as from causticizing plants, can be burned only in rotary kilns.

The lime in the vertical kiln is partly cooled by the incoming air. It may be taken from the kiln and further cooled. It is packed for shipment as lumps in barrels and drums or shipped in bulk. It may be pulverized before sale. In many plants, instead of disposing of the product as quicklime, it is converted to the hydroxide and sold in the form of slaked or hydrated lime.

GYPSUM

Gypsum is a mineral that occurs in large deposits throughout the world. It is hydrated calcium sulfate, with the formula $CaSO_4 \cdot 2H_2O$. When heated slightly, the following reaction occurs:

$$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot \tfrac{1}{2}H_2O + 1\tfrac{1}{2}H_2O(g); \qquad \Delta H = +19{,}700 \text{ cal.}$$

If the heating is at a higher temperature, gypsum loses all of its water and becomes anhydrous calcium sulfate or "anhydrite." Calcined gypsum can be made into wall plaster by the addition of filler materials such as asbestos, wood pulp, or sand. Without additions, it is plaster of paris and is used for making casts and for plaster.

Calcination of Gypsum.—The usual method of calcination of gypsum consists of grinding the mineral and placing it in a large calciner which holds about 10 tons of gypsum. The temperature is raised to about 350°F. with constant agitation to maintain a uniform temperature. The materials in the kettle, known to the public as *plaster of paris* and to the manufacturer as *first-settle* plaster, may be withdrawn and sold at this point, or it may be heated further to 400°F. to give a material known as *second-settle* plaster. First-settle plaster is approximately the half hydrate, $CaSO_4 \cdot \tfrac{1}{2}H_2O$, and the second form is anhydrous. Practically all of the gypsum plaster sold is in the form of first-settle plaster mixed with sand or wood pulp. The second form is used in the manufacture of plasterboard and other gypsum products. Gypsum may be calcined also in rotary kilns similar to those used for limestone.

Hardening of Plaster.—The hardening of plaster is essentially a hydration reaction, as represented by the equation:

$$CaSO_4 \cdot \tfrac{1}{2}H_2O + 1\tfrac{1}{2}H_2O(l) \rightarrow CaSO_4 \cdot 2H_2O; \qquad \Delta H = -3{,}800 \text{ cal.}$$

This equation is the reverse of that for the dehydration of gypsum. The plaster sets and hardens because the liquid water reacts to form a solid crystalline hydrate. Referring to Fig. 6, it is apparent that hydration with liquid water will take place at temperatures below about 99°C., and that the gypsum must be heated above 99°C. for practical dehydration. Commercial plaster usually contains some glue in the water used or a material such as hair or tankage from the stockyards to retard the setting time in order to give the plasterer opportunity to apply the material.

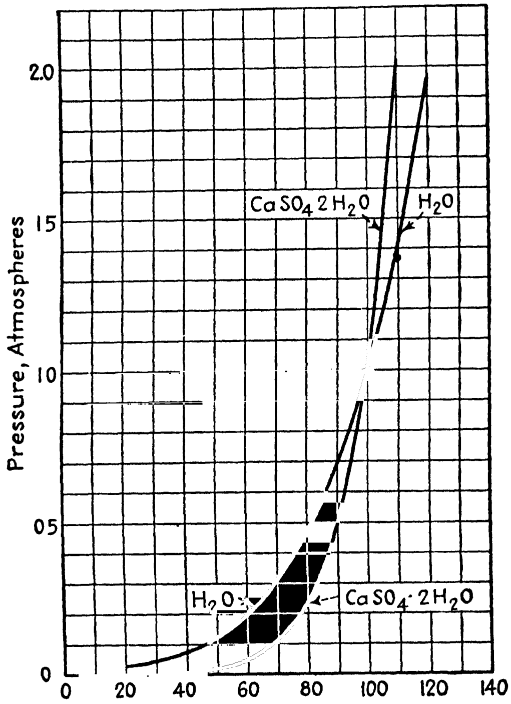

FIG. 6.—Dehydration pressure of gypsum and vapor pressure of water. (*Calculated from Bur. Mines Tech. Paper* 625, 1941.)

MISCELLANEOUS CALCIUM COMPOUNDS

Calcium Carbonate.—Calcium carbonate is a very widely used industrial chemical, in both its pure and its impure state. As marble chips, it is sold in many sizes as a filler in artificial stone, for the neutralization of acids, or for chicken grit. The marble dust is employed in abrasives and in soaps. Some pulverized and levigated limestone, to replace the imported chalk and whiting, is manufactured quite carefully from very pure raw material and is finding acceptance.[1] *Whiting* is pure finely divided calcium carbonate prepared by wet grinding and levigating natural chalk. Whiting mixed with 18 per cent boiled linseed oil furnishes *putty* which sets by oxidation and by formation of the calcium salt. Much whiting also is consumed in the ceramic industry. Precipitated chalk arises through precipitation as by reacting a boiling solution of calcium chloride with a boiling solution of sodium carbonate, or by passing carbon dioxide into a milk of lime suspension. This latter form is used in cosmetics and in tooth paste.

Calcium Sulfide.—Calcium sulfide is made by reducing calcium sulfate with coke. Its main use is as a depilatory in the tanning industry and in cosmetics. In the finely divided form it is employed in luminous paints. Polysulfides, such as CaS_2 and CaS_5 made by heating sulfur and calcium hydroxide, are consumed as fungicides.

Halide Salts.—Calcium chloride is obtained commercially as a by-product of chemical manufacture, principally the Solvay process. For this reason and since large tonnages are available, it is a very cheap chemical. Its main applications are in solutions that are used to lay dust on highways (because it is deliquescent and remains moist) and in low-temperature refrigeration. Calcium bromide and iodide have properties similar to those of the chloride. They are prepared by the action of the halogen acids on calcium oxide or calcium carbonate. They are sold as the hexahydrates for use in medicine and photography. Calcium fluoride occurs naturally as fluorspar. It serves to make hydrofluoric acid, used in glass and steel manufacture.

Calcium Arsenate.—This chemical is produced by the reaction of calcium chloride, calcium hydroxide, and sodium arsenate or lime and arsenic acid.

$$2CaCl_2 + Ca(OH)_2 + 2Na_2HAsO_4 \rightarrow Ca_3(AsO_4)_2 + 4NaCl + 2H_2O$$

There is usually some free lime present (see Chap. XXVI). Calcium arsenate has a large application as an insecticide and as a fungicide. It is especially useful on cotton plants to poison the boll weevil.

Calcium Organic Compounds.—Calcium acetate and lactate are prepared by the reaction of calcium carbonate or hydroxide with acetic or lactic acid. The acetate was formerly pyrolyzed in large amounts to produce acetone but now it is employed largely in the dyeing of textiles. The lactate[1] is sold for use in medicines and in food as a source of calcium; it is an intermediate in the purification of fermentation lactic acid. Calcium soaps such as stearate, palmitate, and the abietate are made by the action of the sodium salts of the acids on a soluble calcium salt such as the chloride. These soaps are insoluble in water but are soluble in hydrocarbons. Many of these form jellylike masses which are a constituent of greases. These soaps are used mainly as waterproofing agents.

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[1] TURNER, "Condensed Chemical Dictionary," 3d ed., Reinhold Publishing Corporation, New York, 1942. **This book is invaluable for presenting outline specifications for industrial chemicals.**

Sand-lime Brick.—Where a cheap white face brick is desired as for courts in apartment houses and buildings or where sand is more available than clay, the sand-lime brick industry has flourished. These bricks are largely competitive with common bricks and are sold at around the same price. They are manufactured by mixing about 8 per cent of thoroughly hydrated lime with a good grade of sand, pressing this mixture to the shape desired, and hardening in a steam autoclave under about 125 lb. steam pressure for around 8 hr. If the hydrated lime used contains any quicklime, this will eventually hydrate or carbonate with expansion. This has caused cracking in the past. However, the operators of modern sand-lime brick factories have been trained to hydrate the lime completely. Consequently no trouble along this line may be expected from sand-lime brick. The bond holding together the sand particles is a monocalcium silicate.[2]

MAGNESIUM OXYCHLORIDE CEMENT

This cement, discovered by the French chemist, Sorel, and sometimes called *Sorel's cement,* is produced by the exothermic action of a 20 per cent solution of magnesium chloride on magnesium oxide or magnesia obtained by calcining magnesite.

$$3MgO + MgCl_2 + 7H_2O \rightarrow 3MgO{\cdot}MgCl_2{\cdot}7H_2O$$

The product is hard and strong but is attacked by water. Its main use is as a flooring cement with an inert filler and a coloring pigment. The surface should be protected against water by polishing with wax or turpentine. Care should be taken in its use because it has a strongly corrosive action on iron pipes laid in or passing through it. Sand and wood pulp may be added as fillers. The expense of these cements restricts their use to special purposes. They do not reflect sound. They can be made sparkproof[3] and as such have been widely employed in ordnance plants.

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[1] See Fig. 9 of Chap. XXXI.

[2] EMLEY, Manufacture and Properties of Sand-Lime Brick, *Nat. Bur. Standards Tech. Paper* 85, Washington, 1917.

[3] SEATON, Magnesium Oxychloride Spark-proof Floors, *Chem. Industries,* **51,** No. 1, 74 (1942).

Recently, an entirely new form of magnesium oxychloride cement, prepared by the addition of 10 per cent of finely divided metallic copper to the mixture, has been developed. The copper ends up in the cement as artificial atacamite, $CuCl_2 \cdot 3Cu(OH)_2$. This material is much more weather resistant than the ordinary hydrated magnesium oxychloride The cement so produced is highly insoluble in water and is free from excessive expansion; its strength when dry is nearly twice, and when wet nearly three times, that of the ordinary magnesium oxychloride cement.[1] The adhesive power to portland cement and similar materials is excellent even in thin layers.

MAGNESIUM COMPOUNDS

Although magnesium is one of the most widely distributed elements (occupying 1.9 per cent of the earth's crust), it has never been found in the elemental form, but usually as the chloride, silicate, hydrated oxide, sulfate, or carbonate, either in complex or simple salts. Magnesium metal first became available commercially shortly before 1914 when the Germans initiated production, using magnesium chloride[2] from the Stassfurt deposits as the raw material. In 1915, consumption of the metal[3] in the United States was 87,500 lb., at an average price of $5 per pound. Table 9 gives recent production figures for magnesium and its compounds.

Raw Materials and Uses.—Important domestic sources of magnesium salts are sea water, bitterns from salt brines and from sea brine, salines, dolomite, and magnesite, $MgCO_3$.

The most important and growing consumption of magnesium compounds is for the production of metallic magnesium (*cf.* Chap. XVI). Magnesium compounds are used extensively for refractories and insulating compounds as well as in the rubber, printing ink, pharmaceutical, and toilet industries.

Manufacture.—The manufacture of magnesium compounds from salines has long been successful in Germany. Recently, as the result of very thorough physical and chemical study, the International Minerals and Chemical Corp. is making magnesium chloride from langbeinite[4] by crystallizing out carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$. This double salt is decomposed to furnish residual magnesium chloride of the requisite high purity needed for electrolysis to metallic magnesium.

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[1] HUBBEL, A New Inorganic Cement and Adhesive, *Ind. Eng. Chem.*, **29**, 123–131 (1937). References.

[2] Available as a by-product of the production of potassium salts.

[3] *Cf.* Chap. XVI for manufacture of the metal.

[4] MANNING and KIRKPATRICK, Better Utilization of Mineral Resources through New Chemical Technology, *Chem. & Met. Eng.*, **51**, No. 5, 92 (1944).

The production of magnesium compounds by separation from aqueous solutions may be divided into four processes:

1. Manufacture from sea water without evaporation, using sea water and lime as the principal raw materials. This is done by Dow Chemical Company at Freeport, Tex. (Fig. 3, Chap. XVI), and by Marine Magnesium Products Corporation at South San Francisco (Fig. 7).

TABLE 9.—MAGNESIUM AND RELATED COMPOUND[a]

Products	Quantity produced		Values in thousands of dollars	
	1940	1941	1940	1941
Magnesium, lb.	12,823,633	....	$3,462	
Asbestos, tons	20,060	....	675	
Magnesite (crude), tons	333,166	374,799	2,488	$2,656
Magnesium salts, 1,000 lb.	216,532	274,714	2,453	3,588

[a] Statistical Abstract of United States, 1942, pp. 845–846. Certain of the above figures have increased *greatly* under wartime stimulation. For instance, the production of magnesium metal probably exceeded 350,000,000 lb. in 1943.

2. Manufacture from bitterns or mother liquors from the solar evaporation of sea water for salt. California Chemical Company employs this source, with its plant on San Francisco Bay (Fig. 8).
3. Manufacture from dolomite, instead of lime, and sea water by the Chesny process, with factories operating at Cape May, N.J., and in England (Fig. 9).
4. Manufacture from deep well brines. This is done by Dow Chemical Company at Midland, Mich.

TABLE 10.—COMPOSITION OF SEA WATER[a]
(In grams per liter of sp. gr. = 1.024)

$NaCl$	27.319
$MgCl_2$	4.176
$MgSO_4$	1.668
$MgBr_2$	0.076
$CaSO_4$	1.268
$Ca(HCO_3)_2$	0.178
K_2SO_4	0.869
B_2O_3	0.029
SiO_2	0.008
Iron and alumina, R_2O_3	0.022

[a] CHESNY, Magnesium Compounds from Ocean Water, *Ind. Eng. Chem.*, **23**, 383 (1936).

A typical analysis of sea water is given in Table 10. The production of magnesium compounds from sea water is made possible by the almost total insolubility of magnesium hydroxide in water. The successful obtaining of magnesium compounds by such a process depends upon *a.* The means to soften the sea water cheaply.

b. The preparation of a purified lime slurry of proper characteristics.

c. The economical removal of the precipitated hydroxide from the large volume of water.

d. The inexpensive purification of the hydrous precipitates.

e. The development of means to filter the viscous slimes.[1]

The reactions are

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCl_2$$
$$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaSO_4$$

Figure 7 shows[2] a flow sheet of magnesium products from sea water. This process specializes in producing such fine chemicals and pharmaceuticals as milk of magnesia and several basic magnesium carbonates such as $3MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ for tooth powders and antiacid remedies, for coating of table salt to render it noncaking, and for paint fillers. Certain of these basic magnesium compounds are also employed with rubber accelerators.

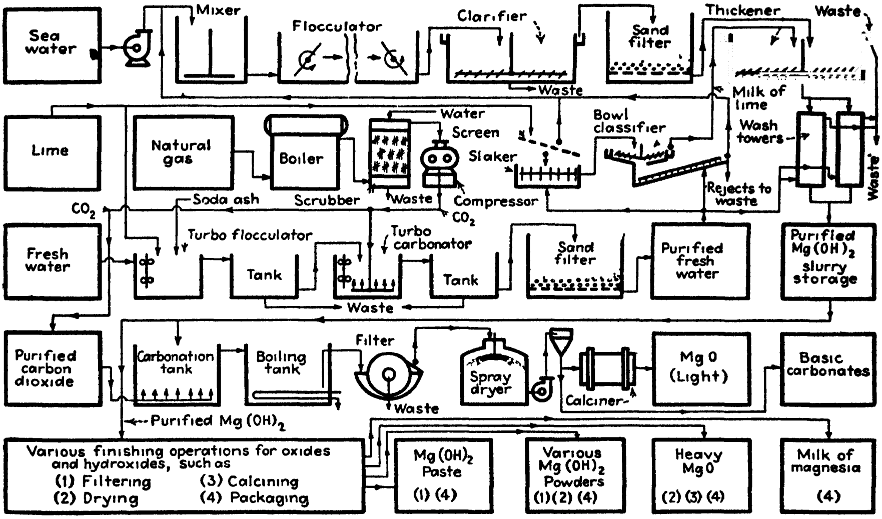

FIG. 7.—Magnesium products from sea water. (*Courtesy of Marine Magnesium Products Corporation.*)

The Dow Chemical Company of Freeport, Tex., also manufactures magnesium compounds[3] directly from sea water using lime. This is employed to make magnesium hydrate which is dissolved in 10 per cent hydrochloric acid to furnish a solution of magnesium chloride. This is concentrated in direct-fired evaporators followed by shelf driers, producing 76 per cent magnesium chloride ready to be shoveled into the electrolytic cells to make metallic magnesium (see Fig. 3 of Chap. XVI).

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[1] CHESNY, Magnesium Compounds from Ocean Water, *Ind. Eng. Chem.*, **28**, 384 (1936).

[2] MANNING, Magnesium Production from Sea Water, *Chem. & Met. Eng.*, **45**, 482 (1938); CHESNY, *op. cit.*

[3] ANON., Magnesium from Sea Water, *Chem. & Met. Eng.*, **48**, No. 11, 130 (1941), pictured flow sheet and description; MURPHY, Magnesium from the Sea, *Chem. Indus-*

Figure 8 presents a flow sheet for the manufacture of magnesium products (and gypsum) from the bitterns or mother liquors from the evaporation of sea water to obtain salt, as practiced by the California Chemical Company on the south part of San Francisco Bay. The bittern is first chlorinated to recover the bromide (not shown). The flow sheet depicts first the removal of gypsum by the reaction:

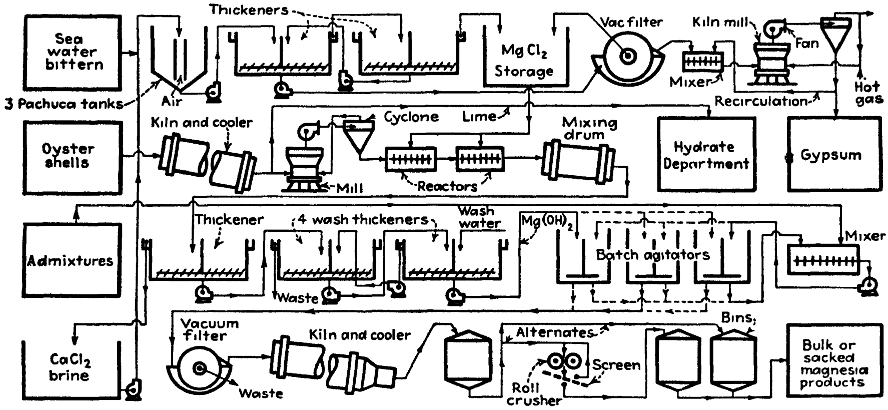

FIG. 8.—Magnesium products from bitterns. (*After the process of the California Chemical Company or Westvaco Chlorine Products Corporation.*)

$$MgSO_4 + CaCl_2 + 2H_2O \rightarrow MgCl_2 + CaSO_4{\cdot}2H_2O$$

Such a step is not necessary in those processes based on sea water when the dilution is sufficient to hold the $CaSO_4$ in solution. Oyster shells dredged from San Francisco Bay yield, upon calcination, a pure lime. This is ground, air-separated, and then hydrated in the presence of the purified bittern, to produce an amorphous $Mg(OH)_2$ which is thickened, washed, filtered, calcined, and sold as magnesia, MgO.

The Chesny process at Cape May, N. J., and elsewhere, uses dolomite instead of calcium carbonate; therefore, approximately only one-half of the magnesia must come from the magnesium salts in the sea water.[1]

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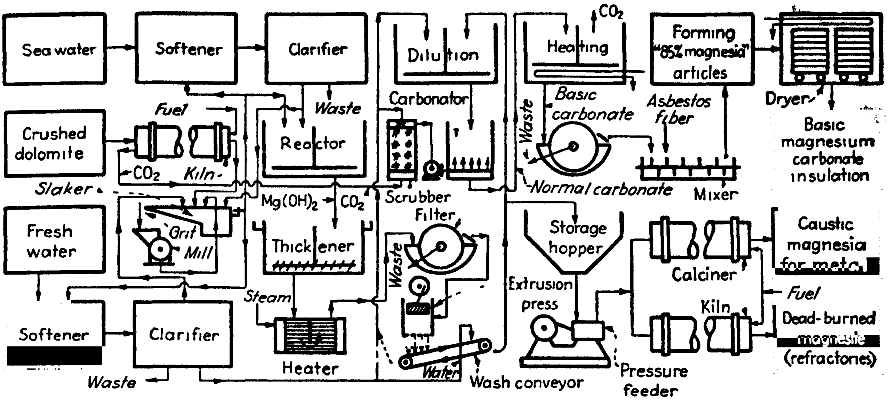
tries, **49**, 618–628 (1942), flow sheet and description; PANNELL, Magnesium Chloride, *Chem. & Met. Eng.*, **48**, No. 1, 81 (1941).

[1] Sea water has normally 2.2 grams per liter of equivalent MgO, actually present as $MgCl_2$ and $MgSO_4$. Hence for 1 ton of MgO there is required theoretically 111,000

Consequently the size of the plant is much smaller, and the cost of production is probably lower.



Sea water	58,000	Gal	Steam	800 lb	Per ton washed Mg (OH)₂
Dolomite	1.7	Tons	Electricity	30 Kw hr	(Dry basis) before conversion
Fresh water	500	Gal	Direct labor	0.66 Man hr	to final products

FIG. 9.—Flow chart for Chesny process for magnesium products from sea water and dolomite.

The reactions, as illustrated in the flow sheet of Fig. 9, are principally the following:

Calcination:

$$2CaMg(CO_3)_2 \rightarrow 2CaO + 2MgO + 4CO_2$$

Slaking:

$$2CaO + 2MgO + 4H_2O \rightarrow 2Ca(OH)_2 + 2Mg(OH)_2$$

Precipitation:

$$2Ca(OH)_2 + 2Mg(OH)_2 + MgCl_2 + MgSO_4 \rightarrow 4Mg(OH)_2 + CaCl_2 + CaSO_4$$

Calcination:

$$4Mg(OH)_2 \rightarrow 4MgO + 4H_2O$$

Only about 7 per cent of the slaked calcined dolomite is needed for softening the sea water, the rest precipitating a crystalline magnesium hydroxide which is easily filtered and washed. This magnesium hydroxide is dissolved in hydrochloric acid and evaporated to make the chloride for the metal.

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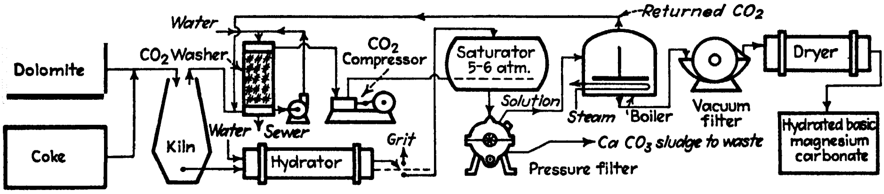
gal. of sea water. Based on a 70 per cent yield, there would be pumped about 158,000 gal. if all the magnesia comes from the sea water, or about half this gallonage if dolomite is used.

The dead-burned magnesia produced does not spall; *e.g.*, bricks made with it do not flake off upon heating and cooling. This magnesium oxide can withstand the temperature of 1750°C. under load, thus permitting a high temperature in the steel open-hearth furnace. The basic magnesium carbonate,[1] usually $3MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$, is made by diluting the washed $Mg(OH)_2$, reacting it with CO_2 from the dolomite calcination, and heating it to release some of the CO_2 and form the basic salt. This is then mixed with 15 per cent asbestos, cast into the desired shapes, and dried for the market as "85 per cent magnesia" insulation.



Note: some manufacturers press the wet basic carbonate into blocks which are then dried and ground. If the basic carbonate is to be used in "85 per cent magnesia" insulation, it is mixed before drying with asbestos fiber, after which it is moulded into blocks and dried. The dried carbonate may be calcined if light burnt MgO is desired. The hydrated basic magnesium carbonate produced has the formula: $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$.

Dolomite	2 tons	Electricity	300 Kw.-hr.	To produce 1 ton basic magnesium carbonate
Coke	0.2 tons	Labor	variable	
Water	18 tons	Steam	9 tons	

FIG. 10.—Basic magnesium carbonate from dolomite.

Magnesium Carbonates.—These vary from dense $MgCO_3$ used in magnesite bricks to the very low density $3MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ or $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$ employed so extensively for insulation. There are also other basic carbonates on the market, as described by Chesny,[2] with variations in adsorptive index and apparent density. Many of these are employed as fillers in inks, paints, and varnishes (see Fig. 9 for manufacture). The basic carbonate is also made from dolomite alone by the procedures in Fig. 10 which depend on calcining the dolomite and dissolving the $Mg(HCO_3)_2$ away from the $CaCO_3$ by treatment with CO_2 under pressure. The $Mg(HCO_3)_2$ is boiled to drive off some CO_2 and form the basic carbonate.

Oxides and Hydroxide of Magnesium.[2]—On heating magnesium carbonate or hydroxide, magnesium oxide, MgO, is formed. This oxide has many uses, such as in the vulcanization of rubber, as a material for making other magnesium compounds, as an insulating material, as a refractory material, and as an abrasive. The magnesium hydroxide,

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[1] See CHESNY, *op. cit.*, p. 388, where detailed reactions are presented.

[2] *Ibid.*, pp. 388–389. See Chap. XVI for the very large manufacture of MgO for $MgCl_2$ for Mg by the process of Basic Magnesium, Inc.

$Mg(OH)_2$, is now made directly from sea water as Fig. 7 shows. After purification this is the well-known milk of magnesia used in medicine. See also the flow charts depicted in Figs. 8 and 9. Magnesium peroxide is available from the reaction of magnesium sulfate and barium peroxide. It is employed as an antiseptic and as a bleaching agent.

Magnesium Sulfate.—Commercially, this is prepared by the action of sulfuric acid on magnesium carbonate or hydroxide. It is sold in many forms, one of which is the hydrate, $MgSO_4{\cdot}7H_2O$, long known as *epsom salt.* The less pure material is used extensively as sizing and as a fireproofing agent.

Magnesium Chloride.—As would be expected, this salt is made from hydrochloric acid and magnesium carbonate, hydroxide or oxide, although it occurs in brines and salines in nature from which commercial amounts are obtained directly. The compound itself much resembles calcium chloride and has many of the same uses. In addition, it finds application in ceramics, in the sizing of paper. and in the manufacture of oxychloride cement. The present large consumption is in making metallic magnesium. Its manufacture is described earlier in this chapter and in Chap. XVI as a step in the making of metallic magnesium. In the latter reference the reaction is:

$$MgO + C + Cl_2 \xrightarrow{850°C.} MgCl_2 + CO$$

Magnesium Silicates.—A consideration of magnesium silicates[1] includes two widely used naturally occurring compounds: asbestos and talc. Asbestos is a magnesium silicate mixed with varying quantities of silicates of calcium and iron. It is a fibrous, noncombustible mineral and is used in the manufacture of many fireproof and insulating materials. Talc is a rather pure magnesium silicate in the form of $3MgO{\cdot}4SiO_2{\cdot}H_2O$ which is found naturally in soapstone. It is employed as a filler in paper and plastics and in many cosmetic and toilet preparations.

Magnesium Soaps.—Magnesium soaps in general are prepared in the same way and have the same properties as calcium soaps. An additional use of magnesium stearate is as a drier in protective coatings.

Problems

1. Draw a flow sheet for a plant manufacturing portland cement by the wet process. All units should be numbered or otherwise designated and a concise, accurate description of each type of unit given in an appendix.

2. A portland cement contains 4 moles of tricalcium silicate to 3 moles of dicalcium silicate. If there are 23.03 lb. of SiO_2 per 100 lb. of cement, what are the absolute amounts of the silicates present? How much CaO should be added to change the ratio to 8 moles of tricalcium silicate to 1 mole of dicalcium silicate?

3. A limestone containing 48 per cent CO_2 (dry basis) and no other volatile material is burned with a coal containing 78.1 per cent C, 6.2 per cent H, 6.2 per cent ash, and 9.5 per cent O_2. The air is dry. Barometric pressure is 757 mm. The stack gases, leaving at 650°F. and 757 mm., contain 26.3 per cent CO_2, 2.9 per cent O_2, and 70.8 per cent N_2. Calculate

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[1] *Cf.* Phase diagram of the system: MgO-SiO_2 in Chap. X.

a. Pounds of lime produced per pound of coal fired.

b. Percentage of excess air.

c. Cubic feet of stack gas per pound of lime produced.

4. In the calcination of pure $CaCO_3$, the CO_2 leaves the kiln at 400°C. The CaO is withdrawn at 1500°C. If the charge enters at 70°C., how many B.t.u. are necessary for complete calcination of 500 lb. of $CaCO_3$? Specific heat of CaO is 0.22 cal. per gram-°C.

5. The gases from a shaft limekiln, externally fired, are 20.0 per cent CO_2, 5.0 per cent O_2, and 75.0 per cent N_2, and leave at 400°F. The coal fired has a heating value of 13,000 B.t.u. per lb. and contains 79.0 per cent C, 6.0 per cent H, 7.5 per cent O, and 7.5 per cent ash. The limestone enters at 70°F. and its analysis is 81.0 per cent $CaCO_3$, 6.0 per cent $MgCO_3$, and 13.0 per cent inert. The burnt lime leaves at 500°F. The entering air is at 70°F. with a water vapor pressure of 12 mm. The barometric pressure is 755 mm. Calculate

a. Pounds of burnt lime produced per pound of coal fired.

b. Percentage of excess air.

c. Sensible heat in waste gases (as percentage of heating value of coal burned).

d. Latent heat in waste gases (as percentage of heating value of coal burned).

e. Heat of decomposition of lime (as percentage of heating value of coal burned).

f. Sensible heat in the lime (as percentage of heating value of coal burned).

g. Radiation and other losses (as percentage of heating value of coal burned).

Heat of formation of $MgCO_3$ from MgO and CO_2 at 70°F.
= 47,300 B.t.u. per lb.-mole

Heat of formation of $CaCO_3$ from CaO and CO_2 at 70°F.
= 76,500 B.t.u. per lb.-mole

Specific heat of burnt lime = 0.18 B.t.u. per lb. per °F.

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CHAPTER XII

GLASS INDUSTRIES

Glass has three important properties that have made it indispensable as a building material in modern civilization: its hardness, its transparency, and its chemical resistance. To these should be added refractive and dispersive powers, compressive and tensile strengths, as well as coefficient of expansion. Whatever has been done in recent years to extend the usefulness of glass has depended largely upon the ability of the glass technologist to vary and control these essential properties, particularly the three first named.

History.[1]—Like many other commonplace materials of our modern civilization, the discovery of glass is very uncertain. One of the earliest references to this material was by Pliny, who related the familiar story of how some ancient Phoenician merchants discovered it while cooking a meal in a vessel placed accidentally upon a mass of trona at the seashore. The union of the sand and alkali caught the men's attention and led to subsequent efforts at imitation.

As early as 6,000 or 5,000 B.C. the Egyptians were making sham jewels of glass which were often of fine workmanship and marked beauty. During medieval times Venice enjoyed a monopoly as the center of the glass industry; and, it was not until the sixteenth century that any glass was made in either Germany or England. Window glass is mentioned as early as A.D. 290. The hand-blown window-glass cylinder was invented by a twelfth-century monk. However, it was not until the fifteenth century that the use of window glass became general. Plate glass appeared as a rolled product in France in 1688.

The first glassworks in America were founded at the beginning of the seventeenth century at Jamestown in 1608 and at Salem, Mass., in 1639. For more than three centuries after it had been established in America, the glass industry remained essentially stagnant as far as technological advance was concerned. The processes were practically all manual and rule of thumb. From the chemical point of view, the only major improvements during this period were confined to purifying the batch materials and increasing the economy in fuel. To be sure, some relations were established between the chemical composition of glasses and their optical and other physical properties but, all in all, the industry prior to 1900 was an art, with closely guarded secret formulas and empirical processes of manufacture based primarily upon experience.

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[1] SILVERMAN, Glass, What Is Old, What Is New? *Ind. Eng. Chem.*, **32**, 1415 (1940).

Toward the end of the nineteenth century Lubbers invented a mechanical adaptation of the hand-blown window-glass cylinder process, and in 1914 the Fourcault process for drawing a sheet of glass continuously was developed in Belgium. These were followed by other direct continuous-sheet processes, including the Colburn, Pittsburgh Plate Glass, and Libbey-Owens processes. The advent of the closed automobile created an enormous demand for small sizes of plate glass, which was partly met by the entrance of the automobile manufacturers themselves into this manufacture. Meanwhile, nearly all branches of the industry were in process of rapid evolution. Scientists and engineers entered the field in increasing numbers. Automatic machines were invented to speed up production of bottles, light bulbs, etc., and new products appeared as the result of intensive research. As a result, today the glass industry is a highly specialized field employing all the tools of modern science in the production, control, and development of its many products.

Uses and Economics.—The production of glass and glassware in the United States amounts to considerably more than a quarter of a billion dollars annually, with an aggregate volume of some 3,000,000 tons, and may be classified under three major headings, with distribution as follows: glass containers, 45 per cent; flat glass, 30 per cent; all others, such as tableware, illuminating ware, and scientific glass, 25 per cent. Imports amount to only about 2 per cent of domestic production, and exports are slightly in excess of imports. The glass and glassware production by types is shown in Table 1. The uses and applications of glass are very numerous but some conception of the versatility of this material can be gained from the discussion of the various types, as described in the rest of this chapter.

TABLE 1.—GLASS AND GLASSWARE[a]

	Value, 1937	Value, 1939
Glass and glass products, aggregate	$354,038,944	$320,405,252
Flat glass	100,938,681	71,385,597
Glass containers	162,206,674	156,364,837
Glassware, n.e.c	90,893,589	92,654,818

[a] *Chem. & Met. Eng.*, **48**, No. 2, 114 (1941).

MANUFACTURE

Glass may be defined: *physically* as a rigid, undercooled liquid having no definite melting point and a sufficiently high viscosity (greater than 10^{13} poises) to prevent crystallization; *chemically* as the union of the nonvolatile inorganic oxides resulting from the decomposition and fusing of the alkali and alkaline earth compounds, sand, and other glass constituents. Glass is a *completely vitrified* product or at least such a product with a relatively small amount of nonvitreous material in suspension.

TABLE 2.—CHEMICAL COMPOSITION OF TYPICAL GLASSES[a]
(In per cent)

No.	SiO_2	B_2O_3	Al_2O_3	Fe_2O_3	As_2O_3	CaO	MgO	Na_2O	K_2O	PbO	SO_3
1	67.8	.....	4.4	....	....	4.0	2.3	13.7	2.3	....	1.0
2	69.4	...	3.5	1.1	....	7.2	....	17.3			
3	70.5	....	1.9	0.4	.	13.0	....	12.0	1.9		
4	71.5		1.5	.	..	13.0	....	14.0			
5	72.88		0.78		...	12.68	0.22	12.69			
6	72.9	....	0.7		....	7.9	2.8	15.0			
7	72.68	.....	0.50	0.07	....	12.95	....	13.17	.....	....	0.44
8	74.50	.....	0.81	0.09	....	5.5	4.1	15.0			
9	72.4	.....	0.8	0.4	....	5.3	3.7	17.4			
10	73.88	16.48	2.24		0.73	.....	....	6.67	Trace		
11	74.2	0.4	....	....	0.2	4.3	3.2	17.7			
12	67.2	.....	....	....	0.5	0.9	....	9.5	7.1	14.8	
13	69.04	0.25	....	....	....	12.07	....	5.95	11.75		
14	64.7	10.6	4.2	....	....	0.6	....	7.8	0.3		
15	80.75	12.00	2.20		0.40	0.30	....	4.10	0.10		
16	80.9	12.6	1.8	....	....	....	....	4.4			
17	96.0	3.6									

[a] Data from either Sharp, Chemical Composition of Commercial Glasses, *Ind. Eng. Chem.*, **25**, 755 (1933) or Blau, Chemical Trends, *ibid.*, **32**, 1420 (1940).

1. Egyptian from Thebes (1500 B.C.) (Blau).
2. Pompeian window (Blau).
3. German window (1849) hand-blown (Blau).
4. Representative window and bottle glass of nineteenth century (Sharp).
5. Machine cylinder glass (Sharp).
6. Fourcault process sheet with 0.7 per cent BaO (Sharp).
7. Polished plate with 0.18 per cent Sb_2O_3 (Sharp).
8. Owens machine bottle (Sharp).
9. Electric light bulb (Sharp).
10. Jena, incandescent gas chimney (Sharp).
11. Tableware, lime crystal (Sharp).
12. Tableware, lead crystal (Sharp).
13. Spectacle with 0.9 per cent Sb_2O_3 (Sharp).
14. Jena with 10.9 per cent ZnO, 1911 laboratory (Sharp).
15. Corning Pyrex laboratory (Sharp).
16. Laboratory Pyrex 774 (Blau).
17. 96 per cent silica No. 790 (1940) (Blau).

Composition.—In spite of hundreds of new developments in glass during the past thirty years, it is worthy of note that lime, silica, and soda still form over 90 per cent of all the glass of the world, just as they did 2,000 years ago. It should not be inferred that there have been no important changes in composition during this period. Rather, there have been minor changes in major ingredients or major changes in minor ingredients. The major ingredients are sand, lime, and soda ash, and any other raw materials may be considered to be minor ingredients, even though the effects produced may be of major importance. Table 2 shows the chemical composition of various glasses.

In general, commercial glasses fall into six different classes:

1. Vitreous silica—a glass made by fusing pure silica without a flux, and very resistant thermally and chemically.
2. Alkali silicates—soluble glasses used only as solutions.
3. Lime glass—the soda-lime-silica glass of such wide applications, for windows, transparent fixtures, and all manner of containers.
4. Lead glass—the product obtained from lead oxide, silica, and alkali for decorative and optical effects.
5. Borosilicate glass—boric oxide and silica glasses for optical and scientific work.
6. Special glass—such as colored glass, translucent glass, safety and laminated glass, fiber glass, and specialties for chemical uses.

Vitreous silica, sometimes referred to erroneously as *quartz glass,* is the end member of the silicate glasses. It is characterized by low expansion and high softening point, which impart high thermal resistance and permit this to be used beyond the temperature ranges of other glasses. This glass is also extraordinarily transparent to ultraviolet radiation.

The *alkali silicates* are the only two-component glasses of commercial importance. These are water soluble. The sand and soda ash are simply melted together and the products designated as sodium silicates,[1] having a range of composition from $Na_2O \cdot SiO_2$ to $Na_2O \cdot 4SiO_2$. Silicate of soda solution, also known as *water glass,* is widely consumed as an adhesive for paper in the manufacture of corrugated paper boxes. Other uses include fireproofing and egg preservation. The higher alkaline varieties enter into laundering as detergents and as soap builders.

Lime glass represents by far the largest tonnage of glass made today and serves for the manufacture of containers of all kinds, flat glass (window, plate, wire, and figured), tumblers, and tableware. There has been a general betterment in the physical quality of all flat glass such as increased flatness and freedom from waves and strains, but the chemical composition has not varied greatly. This composition as a rule lies between the following limits:[2] (1) SiO_2, 69 to 72 per cent, (2) CaO, 12.5 to 13.5 per cent, (3) Na_2O, 13 to 15 per cent, because products of these ratios do not melt too high and are sufficiently viscous so that they do not devitrify and yet are not too viscous to be workable at reasonable temperatures. The great improvement has been in the substitution of instrument-controlled mechanical devices for the individualism of the hand operator. Similarly in container glass, the progress has been largely of a mechanical nature. However, the influence of the liquor trade has caused a tendency among manufacturers to make glassware particularly high in alumina and lime and low in alkali. This type of glass melts with more difficulty but is more chemically resistant. It might be mentioned in passing that the color of container glass is much better than formerly because of a better selection and purification of raw materials, and the use of selenium as a decolorizer.

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[1] See Chap. XIV for fuller description.

[2] MOREY, p. 781 in "Rogers' Manual of Industrial Chemistry," 6th ed., D. Van Nostrand Company, Inc., New York, 1942.

The applications of phase-rule[1] studies have explained many of the earlier empirical observations of the glassmaker, have led to some improvements such as more exactness in the manufacture of lime glass, and have laid the basis for new glass formulations. The phase diagrams for many systems are known and published, but the system Na_2O-CaO-SiO_2 has been particularly detailed.[2]

Lead glasses are of very great importance in optical work because of their high index of refraction and high dispersion. Lead contents as high as 80 per cent (density 6.4, refractive index 2.0) are used. The brilliancy of good "cut glass" is due to its lead-bearing composition. Large quantities are used also for the construction of electric light bulbs and radiotrons, because of the high electrical resistance of the glass.

The *borosilicates*[3] usually contain about 10 to 12 per cent of B_2O_3, 80 to 83 per cent of silica, and have low expansion coefficients, superior resistance to shock, excellent chemical stability, and high electrical resistance. Wide and ever-increasing uses for these glasses have revolutionized the ideas of the laymen toward the properties of glass. Among the diversified applications of these glasses are baking dishes, laboratory glassware, pipe lines, high-tension insulators, and washers.

The *special glasses* include (1) colored glass, (2) translucent glass, (3) safety or laminated glass, (4) fiber glass, and (5) high-silica glass.

1. Though for many centuries colored glass was used merely for decoration, today colored, transparent glasses are essential for both technical and scientific purposes and are produced in many hundreds

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[1] Lewis, Squires, and Broughton, "Industrial Chemistry of Colloidal and Amorphous Materials," pp. 285–304, The Macmillan Company, New York, 1942; Morey, Phase and equilibrium Relationships Determining Glass Compositions, *Ind. Eng. Chem.*, **25**, 743 (1933); Sharp, Chemicals Composition of Commercial Glasses, *Ind. Eng. Chem.*, **25**, 755 (1933).

[2] Morey, in "Rogers' Manual," pp. 776–781.

[3] Frequently sold under the name of Pyrex.

of colors. Colored glasses are made by the addition of an appropriate agent to the batch or by the precipitation of colloidal particles within an originally colorless glass. Examples of the first are cupric oxide (0.2 per cent CuO) for blue glass, selenium oxide for pink glasses, and cerium and titanium oxides for yellow glasses. An example of the second class of coloring methods is the precipitation of colloidal gold in the glass medium, producing thereby gold ruby glass. It might be noted here that one agent may act differently on different type batches, *e.g.*, NiO dissolved in sodium-lead glass yields a brown color. but in a potash glass it produces a heliotrope. Other coloring agents include neodymium oxide to produce pink, iron chromite for emerald green, cadmium sulfide and selenium dioxide for ruby, and cobalt and cerium oxides for blue glasses.

2. Translucent glasses are clear when molten but become opalescent as the glass is worked into form, owing to the separation and suspension of minute particles in the medium. They are important commercially as diffusing media in illumination, as containers, and as construction material.

3. Safety or laminated glasses may be defined as of a composite structure consisting of two layers of glass with an interleaf of plastic, such as plasticized cellulose nitrate or acetate and polyvinyl butyral resin. When the glass is broken, the fragments are held in place by the interlayer. Recently, developments of England and in America have led to the introduction of a casehardened safety glass, which, with a blow sufficiently hard to break it, disintegrates into many small pieces without the usual sharp cutting edges. The manufacture of safety glass is presented later in this chapter (page 235).

4. Modern fiber glass (*cf.* Chap. XXXIV, Synthetic Fibers), although not a new product, owes its enhanced usefulness to its extreme fineness (of the order of 0.0005 in. and as small as 0.0002 in.). It can be spun into yarn, gathered into a mat, made into insulation, tape, air filters, and a great variety of other products.

5. The making of high-silica glass is considered on page 236.

Raw Materials.—In order to produce all these various glasses, over 2,000,000 tons of glass sand are used in the United States each year. To flux this silica requires over 600,000 tons of soda ash, 45,000 tons of salt cake, and 350,000 tons of limestone or equivalent lime. In addition to these, there is a heavy consumption of lead oxide, pearl ash (potassium carbonate), saltpeter, borax, boric acid, arsenic trioxide, feldspar, and fluorspar, together with a great variety of metallic oxides, carbonates, and the other salts required for colored glass. In finishing operations, such diverse products as abrasives and hydrofluoric acid are consumed.

Sand for glass manufacture should be almost pure quartz. A glass sand deposit has, in many cases, determined the location of glass factories. Its iron content should not exceed 0.045 per cent for tableware or 0.015 per cent for optical glass, as iron affects adversely the color of most glass.

Feldspars have the general formula $R_2O \cdot Al_2O_3 \cdot 6SiO_2$, where R_2O represents Na_2O or K_2O or a mixture of these two. They have many advantages over most other materials as a source of aluminum oxide, because they are cheap, pure, and fusible and are composed entirely of glass-forming oxides. Al_2O_3 itself is used only when cost is a secondary item. Feldspars also supply Na_2O or K_2O and SiO_2. The alumina content serves to lower the melting point of the glass and to retard devitrification.

Borax, as a minor ingredient, supplies the glass with both sodium oxide and boric oxide. Though seldom employed in window or plate glass, borax is now in common use in certain types of container glass. Besides its high fluxing power, borax not only lowers the expansion coefficient but increases chemical durability. Boric acid is used in batches where only a small amount of alkali is wanted. Its price is about twice that of borax.

Salt cake, long accepted as a minor ingredient of glass, and also other sulfates, such as ammonium and barium sulfates, are encountered frequently in all types of glass. Salt cake is said to remove the troublesome scum from tank furnaces. Carbon should be used with sulfates to reduce them to sulfites. *Arsenic trioxide* may be added to facilitate the removal of bubbles. *Nitrates* of either sodium or potassium serve to oxidize iron and make it less noticeable in the finished glass. *Potassium*[1] *nitrate* or carbonate is employed in many of the better grades of table, decorative, and optical glass.

Cullet is the crushed glass from imperfect articles, trim, or otherwise waste glass. It facilitates the melting and utilizes a waste. It may be as low as 10 per cent of the charge or as high as 80 per cent.

Refractory blocks for the glass furnace require special care in manufacture. An example of this is the development of mullite, $3Al_2O_3 \cdot 2SiO_2$, largely made by fusion in an electric furnace from the proper ratio of Al_2O_3 and SiO_2 which may be in certain natural clays. The furnace melt is run out, cast into bricks or special shapes, and annealed. Mullite is exceptionally resistant to the corrosive action of molten glass.

Chemical Reactions.—The chemical reactions involved may be summarized:

$$Na_2CO_3 + aSiO_2 \rightarrow Na_2O \cdot aSiO_2 + CO_2 \qquad (1)$$

$$CaCO_3 + bSiO_2 \rightarrow CaO \cdot bSiO_2 + CO_2 \qquad (2)$$

$$Na_2SO_4 + cSiO_2 + C \rightarrow Na_2O \cdot cSiO_2 + SO_2 + CO \qquad (3)$$

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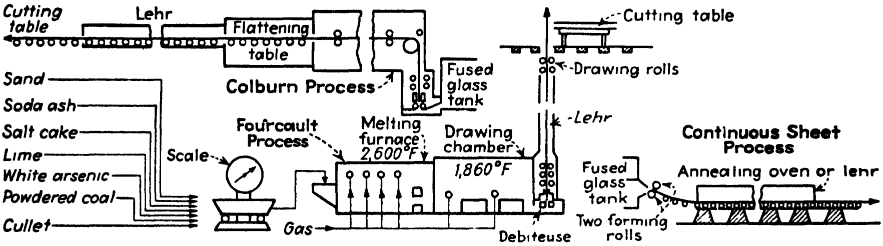
[1] FINN, Potash in the Glass Industry, *Ind. Eng. Chem.*, **30**, 891 (1942).

The last reaction may take place as in equations (4) or (5), and (6):

$$Na_2SO_4 + C = Na_2SO_3 + CO \qquad (4)$$
$$2Na_2SO_4 + C = 2Na_2SO_3 + CO_2 \qquad (5)$$
$$Na_2SO_3 + cSiO_2 = Na_2O{\cdot}cSiO_2 + SO_2 \qquad (6)$$

It should be noted that the ratios Na_2O/SiO_2 and CaO/SiO_2 need not be 1 to 1 molecular ratios. The compounds may be of the type formula $Na_2O{\cdot}1.8SiO_2$ for example. In an ordinary window glass the molecular ratios are approximately: 2 moles Na_2O, 1 mole CaO, 5 moles SiO_2. Other glasses vary widely (see Table 2).



Approximate batch				
	Sand	100 lb.	Lime	15 lb.
	Soda ash, dense	35 lb	Cullet	50 lb.
	Salt cake	10 lb.	Other	1-2 lb.
	Powdered coal	0.5 lb		

FIG. 1.—Flow sheet for flat-glass manufacture.

Unit Operations and Unit Processes.—Typical manufacturing sequences can be broken down into the following *unit operations* (Op.) and *unit processes* (Pr.) (*cf.* Fig. 1):

Transportation of raw materials to plant (Op.).
Sizing of some raw materials (Op.).
Storage of raw materials (Op.).
Conveying to, weighing and feeding raw materials into glass furnace (Op.).
Reacting in furnace to form the glass (Pr.).
Burning of fuel to secure temperature needed for glass formation (Pr.).
Heat saving by regeneration or recuperation (Op.).
Shaping of glass products (Op.).
Annealing of glass products (Op.).
Finishing of glass products (Op.).

To carry out these unit operations and unit processes, the modern glass factories are characterized by the use of materials-handling machinery supplying automatic and continuous manufacturing equipment, in contrast to the "shovel and wheelbarrow" methods of the older factories. In spite of the modernization of many plants, however, manual charging of furnaces is still carried on, though a dusty atmosphere is created. The trend, however, is toward mechanical batch transporting and mixing systems so completely enclosed that practically no dust is emitted at any stage of the handling of glass or raw materials. This is important, because in most states the restrictions against silica dust are becoming more rigorous.

METHODS OF MANUFACTURE

The manufacturing procedures may be divided (*cf.* Fig. 1) into four major phases: (1) melting, (2) shaping, (3) annealing, and (4) finishing.

1. Melting.—Glass furnaces may be classified as either pot or tank furnaces and subclassified as either regenerative or recuperative (*cf.* Fig. 2 of tank furnace).

Pot furnaces are used advantageously for small production of special glasses or where it is essential to protect the melting batch from the products of combustion. They are employed principally in the manufacture of optical glass and of plate glass by the casting process. The pots are really crucibles made of selected clay. It is very difficult to melt glass in these vessels without contaminating the product or partly melting the container itself.

In a *tank furnace* (Fig. 2) batch materials are charged into one end of a large "tank" built of refractory blocks. The glass forms a pool in the hearth of the furnace, across which the flames play alternately from one side or the other. The "fined" glass is worked out of the opposite end of the tank, the operation being continuous. In this type of furnace, as in the pot, the walls gradually wear away under the action of the hot glass. The quality of the glass and the life of the tank are dependent upon the quality of the blocks of construction. For this reason, much study has been given to glass furnace refractories.[1]

Each of the foregoing types of furnaces may be of either regenerative or recuperative design. The *regenerative* furnace operates in two cycles with two sets of checkerwork chambers. The flame gases, after giving up their heat in passing across the furnace containing the molten glass, go downward through one set of chambers stacked with open brickwork or checkerwork, as shown in Fig. 2. A great deal of the sensible heat content of the gases is removed thereby—the checkerwork reaching temperatures ranging from 2600°F., near the furnace, to 1200°F. on the exit side. Simultaneously, air is being preheated by passing up the other previously heated regenerative chamber and is mixed with the fuel gas[2] and burned, the resulting flame being of greater temperature than would have been possible if the air had not been preheated. At regular intervals, the *flow* of air-fuel mixture or the cycle is reversed, entering the furnace from the opposite side, through the previously heated checkerwork, and passing through the original checkerwork, now considerably cooled. The time required for each cycle is 20 to 30 min. Much heat is saved by this regenerative principle and a higher temperature is reached.

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[1] See Refractories, Chap. X; White, Mullite, *Bull. Am. Ceram. Soc.*, **12**, 254 (1933).

[2] If the fuel is producer gas, it is preheated also, but not if a higher B.t.u. type is employed.

Recuperation accomplishes the same effect as regeneration, namely, the preheating of entering air, but the incoming gases flow continuously in one direction only. In a recuperative furnace the hot gases pass through one set of tile passages on their way to the stack, and the air passes through adjacent parallel passages and is preheated as it moves to the furnace. No reversing mechanism is necessary, but disadvantages due to leaking and clogging make it difficult for these furnaces to compete with regenerative furnaces, especially in larger designs.

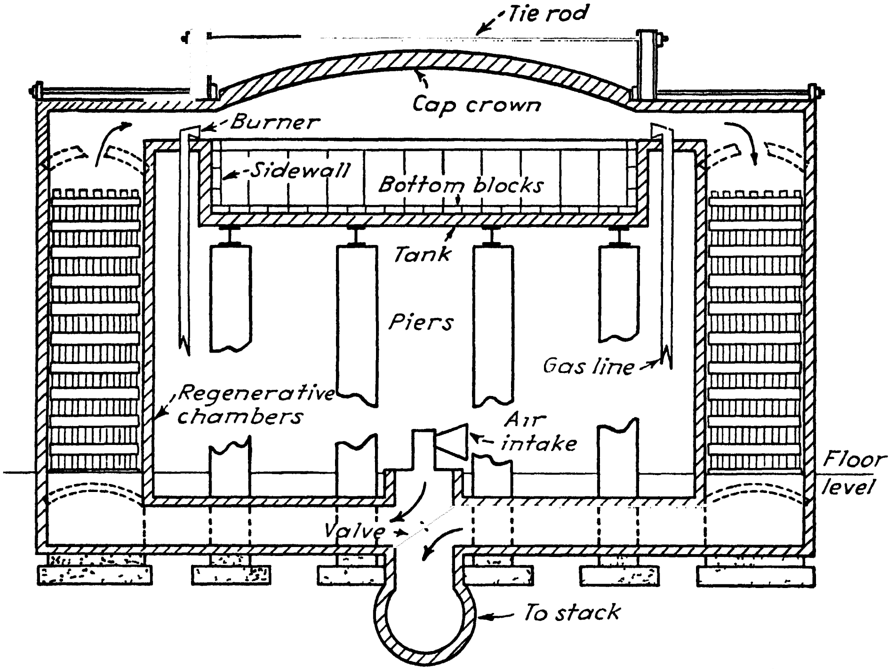

FIG. 2.—Cross section of glass tank furnace showing regenerative chambers.

The temperature of a furnace just entering production can be raised only 150 to 200°F. each day. This is due to the inability particularly of the silica[1] parts of the furnace to stand rapid expansion. Once the regenerative furnace has been heated, a temperature at least of 2200°F. is maintained at all times. Melting cost is about $2 per ton of glass.

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[1] Fire clay, brick, and mullite, however, can withstand more rapid expansion.

The larger part of the heat is lost by radiation from the furnace and the much smaller part is actually expended in the melting. However, unless the walls were allowed to cool somewhat by radiation, their temperature would get so high that the molten glass would dissolve or corrode them much faster. To reduce the action of the molten glass on the furnace wall, water cooling pipes are frequently placed in the furnace wall.

2. Shaping or Forming.—Glass may be shaped by either machine or hand molding. The outstanding factor to be considered in *machine molding* is that the design of the glass machine should be such that the article is completed in a very few seconds. During this relatively short time the glass changes from a viscous liquid to a clear solid. It can, therefore, be readily appreciated that the design problems to be solved, such as flow of heat, stability of metals, and clearance of bearings, are very complicated. The success of such machines is an outstanding tribute to the glass engineer. Following is a description of the most common types of machine-shaped glass, *i.e.*, window glass, plate glass, bottles, light bulbs, and tubing.

Window Glass.—For many years window glass was made by an extremely arduous hand process that involved gathering a gob of glass on the end of a blowpipe and blowing it into a cylinder. The ends of the latter were cut off, the hollow cylinder split, heated in an oven, and flattened. This tedious manual process has now been entirely supplanted by two continuous processes or their modifications, the Fourcault process and the Colburn process, as outlined in the flow sheets of Fig. 1.

In the Fourcault process a drawing chamber is filled with glass from the melting tank. The glass is drawn vertically from the kiln through a so-called *débiteuse* by means of a drawing machine. The débiteuse consists of a refractory boat with a slot in the center through which the glass flows continuously upward when the boat is partly submerged. A metal bait lowered into the glass through the slot at the same time that the débiteuse is lowered starts the drawing as the glass starts flowing. The glass is continuously drawn upward in ribbon form as fast as it flows up through the slot, and its surface is chilled by adjacent water coils. The ribbon, still traveling vertically and supported by means of asbestos-covered steel rollers, passes through a 25-ft.-long annealing chimney or lehr. On emerging from the lehr, it is cut into sheets of the desired size and sent on for grading and cutting. This is shown diagrammatically in Fig. 1.

The Pittsburgh Plate Glass Company operates a modified Fourcault process which produces their Pennvernon glass. These sheets are drawn 90 in. wide and of all thicknesses up to $\frac{7}{32}$ in. by varying the drawing rate from 38 in. a minute for single strength[1] to 12 in. for 7/32 in. This process substitutes for the floating débiteuse a submerged drawbar for controlling and directing the sheet. After being drawn vertically through a distance of 26 ft., most of which is an annealing lehr, the glass is cut. For thicknesses above single and double strength, a second annealing is given in a 120-ft. standard form horizontal lehr.

During 1917 the Libbey-Owens Sheet Glass Company (now Libbey-Owens-Ford Glass Company) began drawing sheet glass by the Colburn process. In this process drawing is started vertically from the furnace, as in the Fourcault process, but after traveling for about 3 ft., the glass is heated and bent over a horizontal roller and is carried forward by grip bars attached to traveling belts. The sheet moves over the flattening table through the horizontal annealing lehr, with its 200 power-driven rolls, onto the cutting table.

Plate Glass.—Previous to the First World War, plate glass was manufactured by pouring the molten charge on a flat, cast-iron table, just ahead of a heavy cast-iron, water-cooled roller which rolled the glass into a plate of uniform thickness. These tables were usually about 16 by 30 ft. and were covered with fine sand to prevent sticking and chilling. The glass was then pushed into a series of five annealing ovens. Great skill and careful timing were required to coordinate the roll speed and rate of pouring so that the glass produced might be rolled smoothly without seams or folds. This process has now been entirely abandoned in favor of several continuous processes.

Between 1922 and 1924 the Ford[2] Motor Company and the Pittsburgh Plate Glass Company each developed a continuous automatic process for removing rough-rolled glass in a continuous ribbon (*cf.* Continuous Sheet Process of Fig. 1). The glass is melted in large continuous furnaces holding about 1,000 tons at a time. The raw materials are fed into one end of the furnace, and the melted glass passes through the refining zone and out of the opposite end in an unbroken flow. From the wide refractory outlet, it passes between two water-cooled forming rolls and travels down an incline onto a table of moving, metal plates, where rollers squeeze the glass into a ribbon of uniform thickness. While still red hot, the sheet passes over conveyer rolls to a continuous annealing lehr several hundred feet in length. The glass is removed from the lehr, cut into sheets, and then sent on for grinding and finishing, as illustrated in Fig. 3.

The continuous processes have very large capacities and are particularly adapted to the production of a glass with a uniform thickness and a composition suited to the requirements of the automobile industry. Short runs of plate or special glass cannot be produced economically by these machines but are handled in pots and mechanically cast by machines made especially for this type of operation.

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[1] Single-strength window glass has a thickness of 0.087 to 0.100 in.; double-strength glass measures 0.118 to 0.132 in.

[2] McBride, Again Ford Shows the Way, *Chem. & Met. Eng.*, **46**, No. 3, 150 (1939).

Bottle Glass.—Glass blowing, one of the most ancient arts, has until the last century depended solely upon human lungs for power to form and shape the molten glass. Modern demands for blown glass, however, have required the development of more rapid and cheaper methods of production.[1]

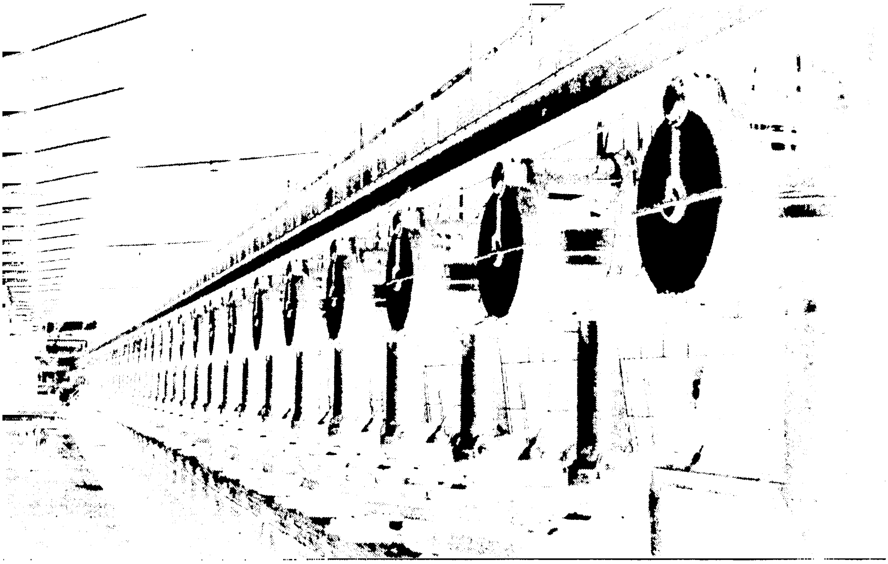

Fig 3—After the rough plate glass comes from the rolls and the annealing lehr, it is ground and polished under many rapidly revolving wheels as it moves along beneath them on a table The glass is embedded in plaster to hold it firmly This view shows the final polishing operation after it has been ground by wheels using successively finer sand mixed with water When one side is finished, the large sheets are turned over and the same operations repeated on the other side The completed glass has both surfaces absolutely parallel, hence the lack of distortion characteristic of plate glass (*Courtesy of Pittsburgh Plate Glass Company*)

The machine making of bottles is really only a casting operation using air pressure to create a hollow. There are several types of machines producing "parisons," the partly formed bottle or bottle blank. One is the suction feed type used, with certain variations, in bulb and tumbler production. Another is the gob feed type, which has been applied to the manufacture of all types of ware made by pressing, blowing, or a combination of "press and blow."

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[1] Hodkin and Cousen, "A Textbook of Glass Technology," D. Van Nostrand Company, Inc., New York, 1929.

In the suction feed type, glass contained in a shallow circular revolving tank is drawn up into molds by suction. The mold then swings away from the surface of the glass, opens, and drops away, leaving the parison

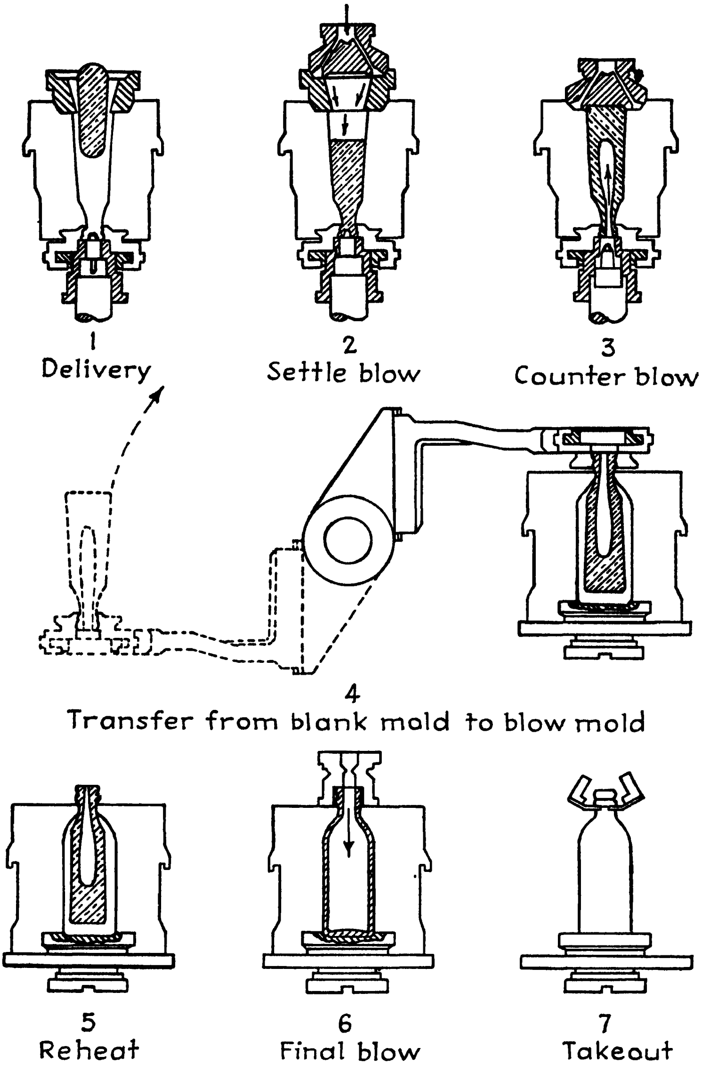

FIG. 4.—Automatic bottle manufacture by I-S machine. (*Courtesy of Glass Packer.*)

sustained by the neck. The bottle mold next rises into position around the parison, and a blast of compressed air flows the glass into the mold. The latter remains around the bottle until another gathering operation has been performed; it then drops the bottle and rises to close around a fresh parison. The operations are completely automatic, and speeds of 60 units per minute are not uncommon.

The gob feeder represents one of the most important developments in automatic glassworking. In this operation the molten glass flows from the furnace through a trough, at the lower end of which is an orifice. The glass drops through the orifice and is cut into a gob of the exactly desired size by mechanical shears. It is delivered through a funnel into the parison mold which starts the formation of the bottle in an inverted position, as shown in Fig. 4. A neck pin rises into place and another plunger drops from the top, whereupon compressed air in the "settle blow" forces the glass to the finished form of the neck. The mold is closed on top (bottom of the bottle), the neck pin is retracted, and air is injected in the "counterblow" through the newly formed neck to form the inner cavity. The parison mold opens and the parison is inverted as it passes to the next station, so that the partly formed bottle is now upright. The blow mold closes around the parison which is reheated for a brief interval. Air is now injected for the final blow, simultaneously shaping the inner and outer surfaces of the bottle. The blow mold swings away and the bottle moves on to the lehr.

Automatic bottle-blowing machines usually consist of two circular tables, known as the *parison mold* table, and the *blow* table. As the glass moves around the periphery of the table, the various operations described above take place. Table movement is controlled by compressed air which operates reciprocating pistons, while the various operations occurring on the table are coordinated with the table movement by a motor-timing mechanism. This latter device constitutes one of the most vital and expensive parts of the equipment.

Light Bulbs.—The blowing of a thin bulb[1] differs from bottle manufacture in that the shape and size of the bulb are determined initially by the air blast itself and not by the mold. The molten glass flows through an annular opening in the furnace and down between two water-cooled rollers, one of which has circular depressions that cause swellings on a glass ribbon coinciding with circular holes on a horizontal chain conveyer onto which the ribbon moves next. Through these holes the glass sags of its own weight. Below each hole is a rotating mold. Air nozzles drop on the surface of the ribbon, one above each of the glass swellings or conveyer holes. As the ribbon moves along, these nozzles eject a puff of air which forms a preliminary blob in the ribbon. The spinning mold now rises and a second puff of air, under considerably less pressure than the first, shapes the blob to the mold and forms the bulb. The mold opens and a small hammer knocks the bulb loose from the ribbon. The bulbs drop onto an asbestos belt which carries them to the lehr rack, where they slip neck down between two parallel, vertical strips which support them as they are annealed. The total time for the entire series of operations, including annealing, is about 8 min. Machine speeds of as high as 450 bulbs per minute are attained. Because of the numerous sizes and styles of bulbs, the machines are assembled as light cars and pushed on rails to the melting tank. The cooled bulbs are frosted by spraying the interior with hydrofluoric acid, in a semi-automatic frosting machine.

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[1] **Killeffer, Automatic Glass Blowing, *Ind. Eng. Chem.*, 28, 789 (1936). This reference includes illustrations and details.**

Glass Tubing.—For many years glass tubing has been drawn by hand and, for certain special tubings, it is still being made in that way. However, most tubing sold today is produced by machines, using either of two processes: the Dannar process[1] or the Vello process. In the Dannar process, glass that has been melted in either a tank or a pot furnace is transferred to a special pot which feeds into a constant-level trough or forehearth. This trough is divided into three compartments by bridges which hold back surface impurities from the molten glass passing through. The flow is controlled by a gate as shown in Fig. 5. The glass escapes over a lip onto the revolving mandrel in the form of a ribbon. The mandrel is a tube of nickel-chrome alloy on which is mounted a sleeve of clay or other refractory material. The mandrel is provided with a nichrome tip (see Fig. 5) and is housed in a muffle heated by a gas burner to a controlled temperature. The inclination of the mandrel (12 to 18 deg.) causes the glass to flow toward the tip from which it is drawn off as a tube or a rod, depending on whether or not air pressure is supplied to the mandrel. The glass passes over pulleys and through an annealing oven for several hundred feet on its way to the drawing machine and the cutter.

In the Vello process[1] molten glass flows into a drawing compartment from which it drops vertically through an annular space surrounding a rotating rod or blowpipe in which air pressure is maintained to produce tubing of the desired diameter and wall thickness.

The drawing of thermometer tubing is one of the most difficult of glass-forming operations. A certain quantity of hot glass is selected, backed on one side with opaque white glass and covered with clear glass, and a small depression is blown in by hand. The end of the composite glass mass is attached to an elevating mechanism and the tube drawn by machinery 125 ft. up a tower.

Glass tower plates and bubble caps, prisms, and most other optical glass, most kitchenware, insulators, certain colored glasses, architectural glass, and many similar items are *hand-molded.* The process consists essentially in drawing a quantity of glass, known as the *gather,* from the pot or tank and carrying it to the mold. Here the exact quantity of glass required is cut off with a pair of shears, and the ram of the mold driven home by hand or by hydraulic pressure. Certain glass forming is carried out by semiautomatic methods which involve a combination of the machine- and hand-molding processes previously described. Volumetric flasks and cylindrical Pyrex sections for towers, some of which are as much as 2 ft. in diameter, are fabricated in this manner.

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[1] PHILLIPS, "Glass the Miracle Maker," pp. 209, 211, Pitman Publishing Corporation, New York, 1941; THORPE, "Dictionary of Applied Chemistry," 4th ed., Vol. 5, p. 589, Longmans, Green and Company, New York, 1941.

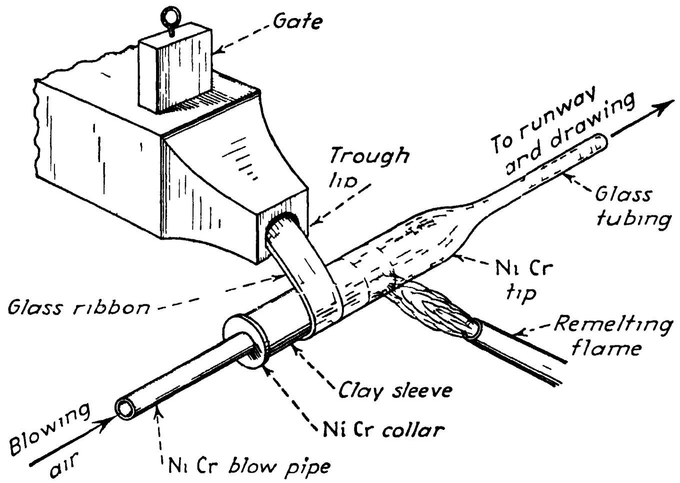

Fig. 5.—Machine (Dannai) for automatically and continuously drawing glass tubing or rods.

3. Annealing.—To reduce strains, it is necessary to anneal all glass objects, whether formed by machine- or hand-molding methods. Briefly, annealing involves two operations: (1) holding a mass of glass above a certain critical temperature long enough to reduce internal strain by plastic flow to less than a predetermined maximum and (2) cooling the mass to room temperature slowly enough to hold the strains below this same maximum. The lehr or annealing oven is nothing more than a carefully designed heated chamber in which the rate of cooling can be controlled so as to meet the foregoing requirements.

The establishment of a quantitative relationship[1] between stress and birefringence caused by the stress has enabled glass technologists to design glass to meet certain conditions of mechanical and thermal stress. With the foregoing data as a basis, engineers have produced continuous annealing equipment with automatic temperature regulation and controlled circulation, which permits better annealing at lower fuel cost and with less loss in product.

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[1] Phillips, *op. cit.*, pp. 223, 121; Morey and Warren, Annealing of Pyrex Chemical Resistant Glass, *Ind. Eng. Chem.*, **27**, 966 (1935); Morey, Physical Tendencies, *Ind. Eng. Chem.*, **32**, 1423 (1940).

4. Finishing.—All types of annealed glass must undergo certain finishing operations, which, though relatively simple, are very important. These include cleaning, grinding, polishing, cutting, sandblasting, enameling, grading, and gaging. Although all of these are not required for every glass object, one or more are almost always necessary.

MANUFACTURE OF SPECIAL GLASSES

Optical Glass.—It should be noted at the very beginning that optical glass[1] includes only those glasses with high homogeneity and special composition which have definite predetermined optical characteristics of such accuracy as to permit their use in scientific instruments. Spectacle glass and ordinary mirror glass are not included.

Optical glass should fill certain rigid requirements: (1) Its composition should be such as to ensure the required optical properties. (2) The batch should produce glass of sufficiently low viscosity. (3) The glass should not devitrify, even upon long annealing. (4) It should produce as nearly a colorless product as possible without the use of decolorizing agents. (5) It should be free from bubbles. (6) Its properties with respect to grinding and polishing should be advantageous. (7) It should be capable of withstanding the action of the atmosphere and of maintaining its surface after long usage under all climatic conditions.

The melting pots for optical glass are made from selected high-purity clays and are of different compositions for different types of glass. The raw materials of the batch are chosen for purity and composition and compounded very carefully. The empty pots are heated slowly for 4 or 5 days, till a temperature of 1900°F. is reached, after which they are transferred to the melting furnace, where they are heated to 2600°F. for several hours before the batch and cullet are charged into them. After the batch has melted, stirring is carried out with a hollow clay tube. The stirring, rapid at first, is gradually reduced after the cooling begins and the glass becomes more viscous. The tube is removed just before the glass is taken from the furnace.

After removal from the furnace, the pot is cooled rapidly to the annealing temperature. The surface of the glass is covered with an insulating powder, while the pot is covered with an insulating drum. The insulation controls the rate of cooling and acts as an annealing furnace. The drum is removed in 3 days, the surface insulation in 4 days, and the pot itself broken away after 5 days. The glass is inspected and broken into small chips, which are further examined by optical instruments. The glass of superior quality is formed into squares by reheating and is then given the final annealing over a period of 2 to 3 weeks. If 20 per cent of the glass from a pot is found usable for making lenses, the run is usually considered to be satisfactory.

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[1] Moulton, Optical Characteristics, *Ind. Eng. Chem.*, **32**, 1428 (1940). Spectral transmission curves.

Safety Glass.—Safety glasses[1] may be grouped into two general classes: laminated safety glass and heat-strengthened or tempered safety glass.

Laminated safety glass, which is by far the most widely used in this country, consists of two sheets of thin plate glass, each of which is about 0.125 in. thick, with a sheet of nonbrittle plastic material between. The manufacturing procedure is somewhat as follows: The plastic and glass are washed, and an adhesive is applied to the glass (if the plastic used requires it, such not always being the case). The glass and plastic sheet are pressed together under moderate heat to seal the edges. Then the glass is subjected to high temperatures and hydraulic pressures in an autoclave, in order to bring the entire interlayer into intimate contact, after which the edges of the sandwich are sealed with a water-resistant compound.

The glass used in the manufacture of laminated safety glass has the same physical properties as ordinary glass; so that the safety features depend solely upon the ability of the plastic interlayer to hold the fragments caused by accidental breaking of the glass itself. The first plastic used commercially was cellulose nitrate. It was relatively unstable to light and heat and became colored. Also, it was quite brittle at low temperatures and lost its adhesion to the glass. By 1939 cellulose acetate had displaced cellulose nitrate very largely as the plastic interlayer, since it was much superior from the standpoint of clarity and stability to light and heat. However, this interlayer was still brittle at low temperatures. After considerable research, polyvinyl butyral (acetal) resin plasticized with either dibutyl sebacate or triethylene glycol dihexoate was found to be superior even to the cellulose acetate. This vinyl acetate plastic is more elastic than the cellulose acetate, since it stretches under relatively low stresses up to its elastic limit, after which considerable additional stress is necessary to make it fail. It remains clear and colorless under all conditions of use and is not affected by sunlight.

The second type of safety glass, tempered safety glass, is considerably more resistant to forces that produce bending and to objects that do not crack or penetrate the compressional layer, but it is weaker to the impact of missiles traveling at sufficiently high velocities to break the compression layer. It is merely a single sheet of glass, heat-treated so that the outer surface is in a state of compression caused by cooling. When the outer layer is punctured, it shatters into many small pieces.

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[1] RANDOLPH, Evolution of Safety Glass, *Modern Plastics*, **18**, No. 10, 31 (1941). *Cf.* WEIDLEIN, History and Development of Laminated Safety Glass, *Ind. Eng. Chem.*, **31**, 563–566 (1939).

High-silica Glass.—Near the end of the First World War, researches in the United States were responsible for important strides in the efforts to produce commercial glasses with properties approaching those of fused silica. These glasses were borosilicates containing slightly over 8 per cent silica and only about 4 per cent alkaline oxides. They were widely used in the fields of laboratory, domestic, and industrial glassware, as a result of their high chemical, electrical, and thermal resistance.

Recently, a new glass[1] has been developed which constitutes an even greater advance toward the production of a glass approaching fused silica in composition and properties. This has been accomplished with the avoidance of former limitations of melting and forming. The finished articles contain approximately 96 per cent silica, the remainder being boric oxide with minor amounts of alumina and alkali. Borosilicate glass compositions of about 75 per cent silica content are used in the earlier stages of the process, in which the glasses are melted and molded.[2] After cooling, the articles are subjected to heat-treatment which induces the glass to separate into two distinct physical phases. One of these phases is so high in boric and alkaline oxides that it is readily soluble in hot acid solutions, while the other is rich in silica and therefore insoluble in these same solutions. After heat-treatment and annealing, the glass article is immersed in a 10 per cent hydrochloric acid (98°C.) bath for sufficient time to permit the soluble phase to be virtually all leached out. It is washed thoroughly to remove traces of the soluble phase as well as impurities and subjected to another heat-treatment which serves to dehydrate the body and to convert the cellular structure to a nonporous, vitreous glass. In the course of these processes the glassware undergoes a shrinkage in linear dimensions amounting to 14 per cent of its original size. Table 3 compares its properties with those of other glasses. This method of glass manufacture furnishes a product that can be heated to a cherry red and then plunged into ice water without any ill effects.

Chemical Engineering Applications.—Glass, because of its reasonable price, its chemical resistance, and the various forms in which it is manufactured, has taken a very important place in industry as an essential chemical engineering material. It is used not only as an all-glass material, such as vessels and pipe, but as a glass lining[1] to steel. By reasons of improvements in the formulas for glass, this material has had its chemical resistance as well as its mechanical properties greatly improved in the past 25 years (see Table 3). Because of these enhanced properties of glass, pumps,[2] condensers, and even bubble-cap towers have been constructed. A special glass product, "foamglas,"[3] is now on the market. It weighs from 10 to 11 lb. per cu. ft. and has a low thermal conductivity of 0.45 B.t.u./(hr.)(sq.ft.)(°F./in.) at 70°F. Fibrous glass[4] is now receiving some commercial acceptance as a packing material for distillation columns.

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[1] This is known as Vycor and is made by the Corning Glass Works. U.S. Pat. 2106744 of Feb. 1, 1938 and 2221709 of Nov. 12, 1940.

[2] PHILLIPS, *op. cit.*, p. 388.

TABLE 3.—COMPARATIVE PROPERTIES OF GLASSES[a]

	Common lime	Pyrex No. 774	96 per cent silica No. 790	Fused quartz
Softening point, °C....	696	819	1442	1667
Annealing point, °C...	510	553	931	1140
Strain point, °C.......	475	510	857	1070
Maximum temperature for use (for limited periods), °C.........	....	500–550	900–1000	1000
Specific gravity.......	2.47	2.23	2.18	2.21
Coefficient of linear expansion............	92×10^{-7}	$32–33 \times 10^{-7}$	$7.8–8 \times 10^{-7}$	$5.5–5.95 \times 10^{-7}$

[a] BLAU, Chemical Trends, *Ind. Eng. Chem.*, **32,** 1419 (1940); *cf.* PERRY, *op. cit.*, p. 2151. The coefficient of linear expansion is the change in length (centimeters) per unit of length (centimeters) per centigrade degree change in temperature.

ROCK WOOL

Allied to the making of glass are the fusing and spinning of a suitable rock to form rock wool. Slag wool is a similar product from the melting of by-product furnace slag. These mineral wools are of great value for both heat and sound insulation, particularly as they have a low coefficient of heat transfer, do not attract moisture, are permanent, and are absolutely fireproof and verminproof. They are also relatively inexpensive and can be fabricated wherever there is the suitable rock available. The mineral wools are employed in the loose form or shaped into blankets for insulating homes or railroad cars. Specially molded sheets or blocks enter into the making of refrigerators. In the loose form, much rock wool is blown into the open spaces in walls and ceilings of already constructed houses. For these purposes 65,000 tons of rock wool are manufactured each year with additional tonnages of slag wool.

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[1] PERRY, *op. cit.*, p. 2151, gives lists of various manufacturers; *ibid.*, pp. 913–916 tabulates sizes of glass pipe and fittings.

[2] THOMPSON, Glass Goes to War, *Chem. Industries*, **51,** 38 (1942). This article is really a listing of the many engineering applications of glass.

[3] FARQUHAR, Glass Cellulation Produces Lightweight Insulation, *Chem. & Met. Eng.*, **50,** No. 8, 98–101 (1943).

[4] MINARD, KOFFOLT, and WITHROW, Fibrous Glass Used in Packing Columns, *Chem. & Met. Eng.*, **51,** No. 2, 145 (1944).

The wool rock[1] should contain silica, alumina, lime, and magnesia approximating the ratio shown in the formula on the flow sheet of Fig. 6, so as to give a product molten over a sufficiently long interval to enable the fibers to be made. To meet these specifications for wool rock there is usually chosen a self-fluxing siliceous and argillaceous dolomite which may have a composition as shown in Table 4. This composition balances the fluxing properties of the constituents. Such natural wool rock is mined in the states of Indiana, Ohio, and elsewhere.

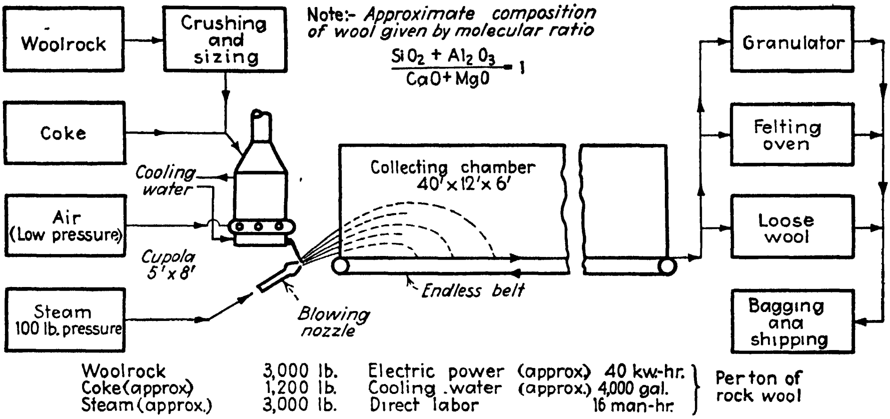

FIG. 6.—Flow sheet for rock or mineral wool.

TABLE 4.—LIMITS OF COMPOSITION OF WOOL ROCK[a]

	Minimum, per cent	Maximum, per cent
Silica	24	32
Ferric oxide	2	3
Alumina	8	12
Calcium oxide	16	21
Magnesium oxide	10	13
Volatile matter	26	29

[a] DAKE, Rock as an Insulator, *Mineralogist*, **10**, 177 (June, 1942).

The process for making rock wool involves the simple melting, in a cupola, of the wool rock at around 3000°F. and the blowing of this into the fibers by means of steam at 100 lb. pressure. The steam first atomizes the molten rock to small globules which stream through the air leaving a fibrous tail behind. The fibers are collected on a belt and subjected to the operations needed to furnish the desired finished wool. Somewhat allied to mineral wool is fiber glass which is presented in Chap XXXIV.

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[1] FRYLING and WHITE, Consideration in Developing a Mineral Wool Industry, *Chem. & Met. Eng.*, **42**, 550 (1935); Mineral Wool, *U.S. Bur. Mines, Circ.* 6984 (1938).

Problems

1. A glass for the manufacture of chemical ware is composed of the silicates and borates of several basic metals. Its composition is as follows:

	Per cent		Per cent
SiO_2	65.0	ZnO	10.8
B_2O_3	8.5	MgO	7.0
Al_2O_3	1.0	Na_2O	7.7

Al_2O_3 acts as a base and B_2O_3 as an acid, HBO_2. Determine whether the acid or basic constituents are in excess in this glass and the percentage of excess reacting value above that theoretically required for a neutral glass.

2. A glass company is producing single-strength (⅛ in. thick) window panes 2½ by 1½ ft. in size. The glass drawn from a débiteuse is 65 in. wide and has a specific gravity of 2.60. What is the largest number of window panes that can be made from a batch of glass of the following weights:

	Tons
Sand (pure SiO_2)	50
Na_2CO_3	16
CaO	7
Na_2SO_4	6
Coal	¼

3. Calculate the percentage of the total charge in the previous problem which disappears from the melt as CO_2 and SO_3.

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CHAPTER XIII

POTASSIUM SALTS AND MIXED FERTILIZERS

Potassium salts must be present in the soil solution in order to have normal plant growth. Hence potassium salts have a high and an essential value in fertilizers needed for the food of the nations. The yardstick by which potassium compounds are measured is the content of potash as K_2O. Indeed, this term has become by usage descriptive of the industry. The various potassium salts are also basically important as raw materials for many commodities such as soaps, glass, dyes, gunpowder, and pyrotechnics.

The establishment of this industry in America has been difficult. Prior to the middle of the nineteenth century the United States was even an important exporter of a crude potassium carbonate from the leaching of hardwood ashes. Potash was first imported from Germany in 1869 and for over 45 years that country furnished America and the rest of the world with potash. After the German salts became available, there was little interest in domestic production of potash until the First World War prevented its importation. At this time the scarcity of potash became a matter of national concern and prices rose to $500 a ton of 50 per cent muriate. Efforts by the Federal, state, and commercial companies developed several sources of potash supply. Among these were brines from the saline lakes in the West, kelp harvested from the Pacific coast, calcined fermentation slop, cement kiln dust, wood and cotton hull ashes, and many minerals of great variety such as alunite, leucite, greensand, feldspar, and shale. Production rose from 1,000 tons in 1915 to 45,000 tons of potash, K_2O, in 1919. When the end of the war came, imports were resumed and domestic production in 1921 fell to 4,400 tons K_2O.

Since that time the discovery of new deposits, followed by new developments in methods of processing, has caused a constant increase in the amount and quality of potash salts produced and in competition with low-priced European imports. In 1939 the United States produced 366,287 short tons of potash, expressed as K_2O, with a total value of $12,028,195, as contrasted with 99,569 short tons imported the same year.[1] Figure 1 presents the movement of potash salts in the United

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[1] *Chemical Facts and Figures*, **1**, 56 (1940), Manufacturing Chemists Assoc., Washington, D.C.

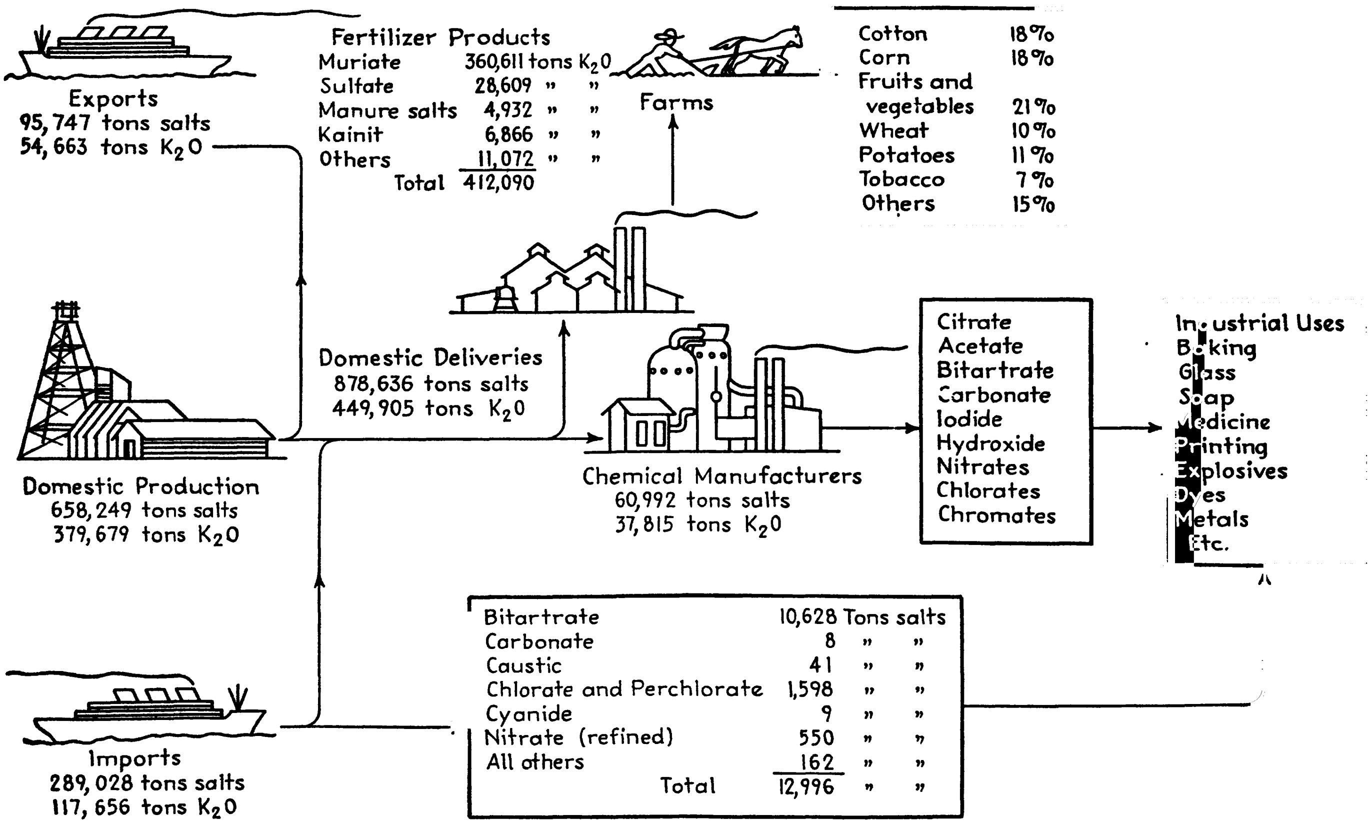

FIG. 1.—The potash industry in 1940. (*Courtesy of American Potash Institute, Inc.*)

States for 1940. In 1941 and in 1942, the United States produced its entire needs for potash for the first time, the figures for 1942 being a production of 1,267,455 tons of the various salts containing 679,206 tons of K_2O with sales 10,000 tons higher and valued at $22,962,518. This satisfying result was achieved only on the foundation of unusually sound phase-rule studies and pioneering engineering. The largest use of potassium salts is as fertilizer materials. However, the following potassium salts find varied industrial application: caustic potash, potassium nitrate, carbonate, bicarbonate, tartrate, chloride, sulfate, chlorate, cyanide, ferricyanide, perchlorate, and permanganate.

Raw Materials.—In the United States two main sources of potassium salts have been successfully developed with large-scale production. One is the mineral sylvinite, a natural mixture of sylvite, KCl, and halite, NaCl, obtained from the Permian salt beds near Carlsbad, N.M. This is mined and processed for the elimination of the sodium chloride constituent to yield high-grade potassium chloride. Occurring in this deposit also is the mineral langbeinite, $K_2SO_4 \cdot 2MgSO_4$, which is being processed for the production of potassium sulfate. The other source is Searlés Lake at Trona, Calif., a deposit of solid salts permeated with a saturated brine. This brine is processed to yield high-grade potassium chloride together with numerous other saline products as described in succeeding paragraphs. Subterranean deposits of potash salts occur in Europe notably in Russia, Poland, Germany, France (Alsace), and Spain. The brine of the Dead Sea in Palestine also is being successfully exploited as a source of potassium chloride.

POTASSIUM CHLORIDE

In this country potassium chloride is being produced principally as a high-grade salt of around 98 per cent purity. As such it is suitable for use in both the chemical and the fertilizer industries, some 90 per cent of the total being used in the latter. In the fertilizer trade it is referred to as *muriate of potash* and in smaller amounts is marketed in the less refined state as "50 per cent muriate," "manure salts," and the crude material as mined, "run-of-mine salts." The refined potassium chloride is the basis of the manufacture of most of the other potassium salts. The four commercial processes in the United States will be described.

Manufacture by the Trona Process.—From Searles Lake, California, the shipment of potash was begun in 1916 and, including numerous other products, has continued since that time on an ever-expanding scale. In this process the brine is pumped from the interstices in the salt body comprising the "lake." This brine has the approximate constant composition:

	Per Cent
KCl	4 70
NaCl	16 35
Na_2CO_3	4 70
Na_2SO_4	6 96
$Na_2B_4O_7$	1 50
Na_3PO_4	0 16
NaF	0 01
Miscellaneous	0 30
Total salts	34 68
H_2O	65 32
Specific gravity	1 30
pH	9 38

As the unraveling of the composition of the various salts of the German potash deposits at Stassfurt by van't Hoff from 1895 to 1910 helped greatly in the development of the German potash industry, likewise the phase-rule study[1] of the much more complex systems existing at Searles Lake by Morse, Teeple, Burke, Mumford, Gale, and many others was another striking investigation carried to a successful application in the Trona process. In the brine of Searles Lake the main system is composed of $Na\text{-}K\text{-}H\text{-}SO_4\text{-}CO_3\text{-}B_2O_4\text{-}Cl\text{-}F\text{-}H_2O$ The references cited, particularly the one by Gale, demonstrate with appropriate solubility charts this important and commercial application of the phase rule wherein the conditions are presented for the desired fractional crystallization.

The phase-rule chemists and the engineers at Trona have been exceedingly clever in obtaining *pure* salts from this complex brine and in building a profitable industry in a competitive field and under the handicap of being in the desert several hundred miles from the nearest city. The town of Trona, Calif., houses over 2,000 inhabitants dependent on this one industry. Figure 2 outlines the steps, based on the phase-rule study, necessary to commercialize this brine. Figure 3 gives more details of the divisions of the procedures leading to potassium chloride, borax, and soda products. There is no profitable market for the large tonnages of common salt obtained, and it is washed back to the lake.

In general this successful process is founded upon many years of intensive research wherein exact conditions were worked out and then applied in the plant. In barest outline this involves the concentration of the potassium chloride and the borax in the *hot* brine with the simultaneous separation of salt and burkeite, a new mineral with the composi-

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[1] TEEPLE, "Industrial Development of Searles Lake Brine," Reinhold Publishing Corporation, New York, 1929, ROBERTSON, The Trona Enterprise, *Ind. Eng. Chem.*, **21**, 520 (1929), ROBERTSON, Expansion of the Trona Enterprise, *Ind. Eng. Chem.*, **34**, 133 (1942); GALE, Chemistry of the Trona Process, from the Standpoint of the Phase Rule, *Ind. Eng. Chem.*, **30**, 867 (1938).

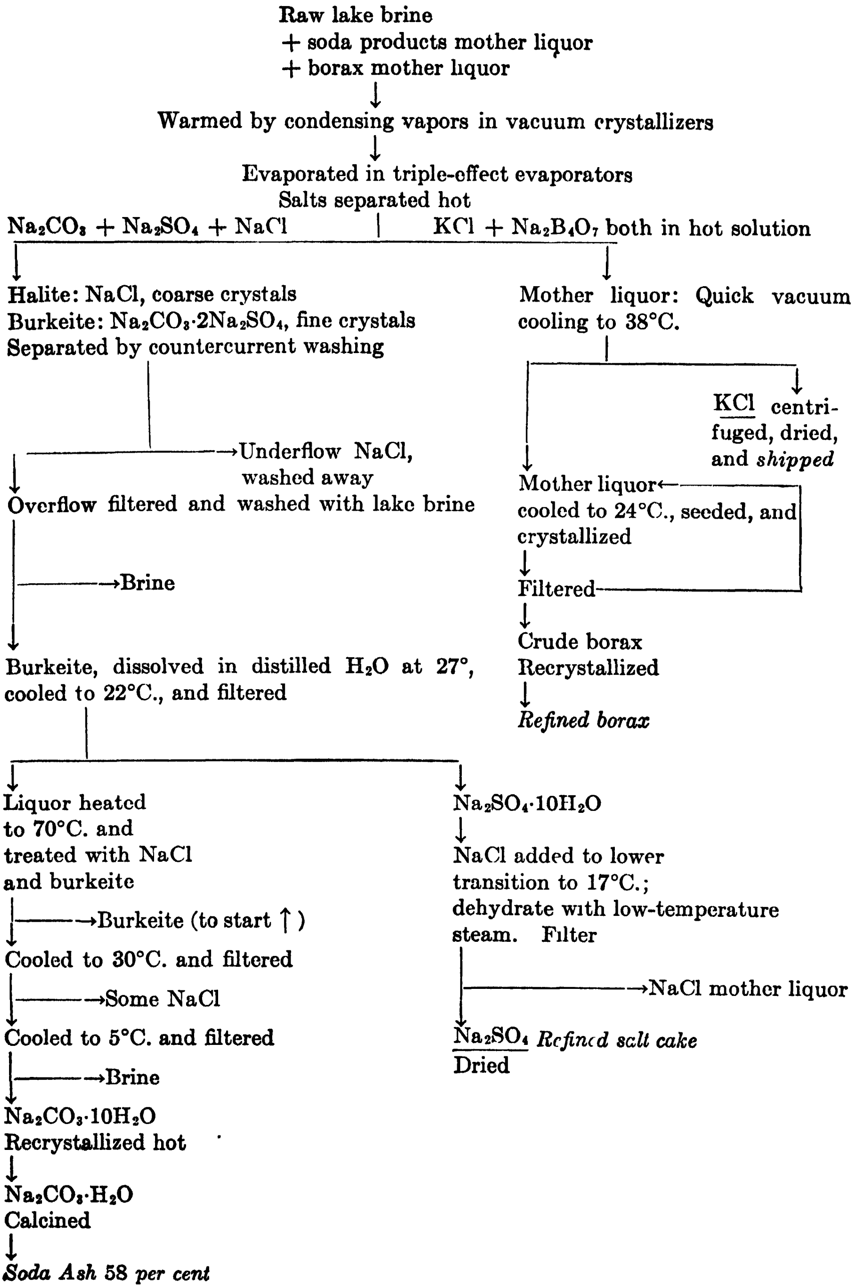
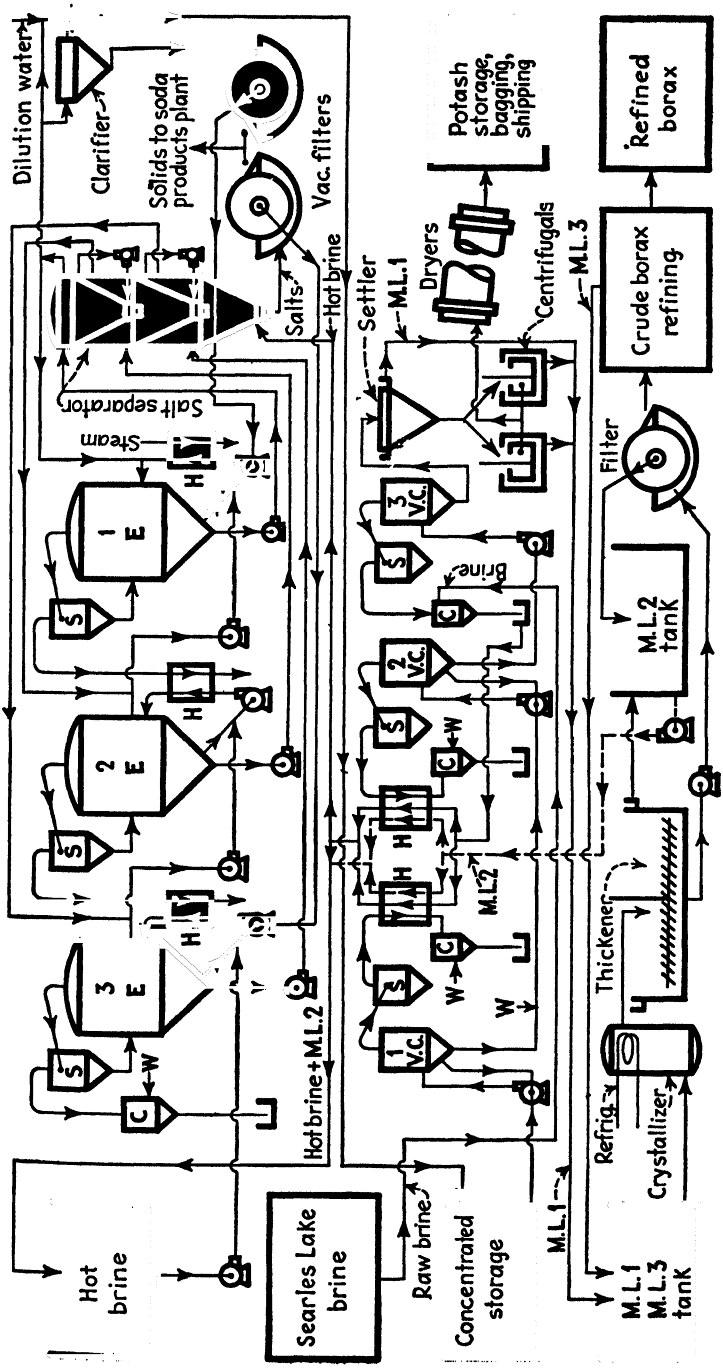

Raw lake brine
+ soda products mother liquor
+ borax mother liquor
Warmed by condensing vapors in vacuum crystallizers
Evaporated in triple-effect evaporators
Salts separated hot
$Na_2CO_3 + Na_2SO_4 + NaCl$
$KCl + Na_2B_4O_7$ both in hot solution
Halite: NaCl, coarse crystals
Burkeite: $Na_2CO_3 \cdot 2Na_2SO_4$, fine crystals
Separated by countercurrent washing
Underflow NaCl, washed away
Overflow filtered and washed with lake brine
Brine
Burkeite, dissolved in distilled H_2O at 27°, cooled to 22°C., and filtered
Mother liquor: Quick vacuum cooling to 38°C.
KCl centrifuged, dried, and *shipped*
Mother liquor
cooled to 24°C., seeded, and crystallized
Filtered
Crude borax
Recrystallized
Refined borax
Liquor heated to 70°C. and treated with NaCl and burkeite
Burkeite (to start ↑)
Cooled to 30°C. and filtered
Some NaCl
Cooled to 5°C. and filtered
Brine
$Na_2CO_3 \cdot 10H_2O$
Recrystallized hot
$Na_2CO_3 \cdot H_2O$
Calcined
Soda Ash 58 *per cent*
$Na_2SO_4 \cdot 10H_2O$
NaCl added to lower transition to 17°C.; dehydrate with low-temperature steam. Filter
NaCl mother liquor
Na_2SO_4 *Refined salt cake*
Dried

FIG. 2.—Outline of Trona procedures.



Key: **C**, Barometric condenser; **E**, Evaporator; **H**, Heater or heat exchanger, **M.L.**, Mother liquor; **S**, Separator; **V.C.**, Vacuum crystallizer; **W**, Cooling or dilution water

FIG. 3.—Potassium chloride and borax by Trona procedure.

tion $Na_2CO_3 \cdot 2Na_2SO_4$. By virtue of the "lazy" crystallization of borax, the potassium chloride can be obtained by the rapid cooling of the concentrated brine in vacuum coolers and crystallizers.[1] After centrifugation the potash mother liquor is refrigerated and furnishes the borax.

The somewhat detailed[2] flow sheet of Fig. 3 can be resolved into the following *unit operations* (Op.) and *unit processes* (Pr.):

Concentration and Soda Products Separation:

Raw brine is mixed with end liquors from the soda products and potash borax crystallizing house, and pumped into the third effect of triple-effect evaporators (Op.).

The brine is hot concentrated with salting out in the three effects counter to the steam flow (Op. and Pr.).

The suspended salts, $NaCl + Na_2CO_3 \cdot 2Na_2SO_4$, are removed from the liquors of each effect by continuously circulating the hot liquor through cone settlers called *salt separators* or *salt traps*. The underflow from the first-effect cone containing the salts passes through an orifice into the second-effect cone, receiving a countercurrent wash with clarified liquor from the second-effect cone. The combined salts from the first and second cones are given a countercurrent wash with liquor from the third cone as they pass through an orifice into this third cone. The combined salts of the first, second, and third cones are given a countercurrent wash with raw brine as they leave the third-effect cone (Op.). All these are hot washes. The combined underflow is filtered and the filtrate returned to the evaporators (Op.).

The cake (salt: NaCl + burkeite: $Na_2CO_3 \cdot 2Na_2SO_4$) is sent to the soda products plant (Op.).

The final hot concentrated liquor is withdrawn from the overflow of the first-effect cone to an auxiliary settler called a *clarifier* (Op.). The overflow from the clarifier is pumped to storage at the potash plant (Op.).

The underflow from the clarifier is filtered and treated in the same manner as the previous underflow[3] (Op.).

Separation of Potassium Chloride:

The hot concentrated liquor leaving the clarifiers is saturated with potassium chloride and borax. The potassium chloride is obtained by cooling quickly to 100°F. and crystallizing in three-stage vaccum cooler-crystallizers (Op. and Pr.).

Enough water is added to replace that evaporated so that the sodium chloride remains in solution (Op.).

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[1] PERRY, *op. cit.*, pp. 1786–1794; see particularly Turrentine, "Potash in North America," pp. 105–107, Reinhold Publishing Corporation, New York, 1943, where the first vacuum cooler-crystallizer is pictured and described. This invention of Turrentine's has had a profound influence upon the cheap production of pure potassium chloride both in the United States and abroad.

[2] MUMFORD, Potassium Chloride from the Brine of Searles Lake, *Ind. Eng. Chem.*, **30**, 872 (1938); KIRKPATRICK, A Potash Industry—At Last, *Chem. & Met. Eng.*, **45**, 488 (1938).

[3] MUMFORD, *op. cit.*, pp. 876, 877.

The suspension of solid potassium chloride in the mother liquor is passed to a cone settler where the thickened sludge obtained in the underflow goes to a battery of Weston-type sugar centrifuges (Op.).

The potassium chloride is dried in rotary driers, yielding 97 per cent KCl (Op.). This salt is conveyed to storage, to the bagging plant, or to a recrystallizing procedure (Op.).

Separation of Borax:

The overflow, combined with the filtrate from the centrifuges, is pumped to the borax plant for the removal of borax (Op.).

The potash mother liquor is cooled by evaporation to 75°F. in vacuum crystallizers by expansion of liquid ammonia in reflux condensers, as shown in Fig. 3 (Op.). The water lost by evaporation is returned to the boiling (but cooling) solution to prevent the concentration of this solution with consequent crystallization of potassium chloride with the crude borax.

The borax crystallizes out (Pr.) and is settled in a thickener (Op.).

The crude borax is filtered off and washed (Op.).

The overflow from the thickener and from the filter is returned to the start of the evaporator cycle (Op.).

When necessary, the crude borax is refined by recrystallization (Op.).

This salt is centrifuged, dried, and packaged for market (Op.).

The Trona plant of the American Potash and Chemical Corporation produces in excess of 500 tons of potassium chloride per day. The daily production of other salts in 1938 amounted to 285 tons of borax, 80 tons of potassium sulfate, 150 tons of soda ash, and 200 tons of sodium sulfate.[1] This large production was not achieved without solving many more problems than those of the phase-rule diagrams. The evaporation is at the rate of 1,930,000 gal. of water per day. To effect the requisite heat transfer when salts crystallize out at the same time was a major chemical engineering problem. This was brought about by removing the miles of piping from the insides of the evaporators and doing the heating in outside heaters arranged with spares around and beneath each evaporator,[2] as shown in Fig. 4.

The *soda products*[3] are a development of recent years by an extension of the phase studies and sound engineering. Figure 2 outlines the production of soda ash and anhydrous sodium sulfate from burkeite, $Na_2CO_3 \cdot 2Na_2SO_4$.

Manufacture from Sylvinite.—In 1925, potash was discovered at Carlsbad, N.M.[4] After much prospecting and drilling, a shaft to mine the mineral was sunk to about 1,000 ft. In 1932 a refinery was constructed and now a very large proportion of the supply of potassium chloride for the United States is being produced here. The ore is sylvinite, which is the accepted term for the natural mixture of sylvite, KCl, with halite, NaCl.

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[1] KIRKPATRICK, *op. cit.*, p. 489.

[2] MANNING, Capital + Vision + Research = An American Potash Industry, *Chem. & Met. Eng.*, **36**, 71 (1929).

[3] ROBINSON, Expansion of the Trona Enterprise, *Ind. Eng. Chem.*, **34**, 133 (1942).

[4] SMITH, Potash in the Permian Salt Basin, *Ind. Eng. Chem.*, **30**, 854 (1938).

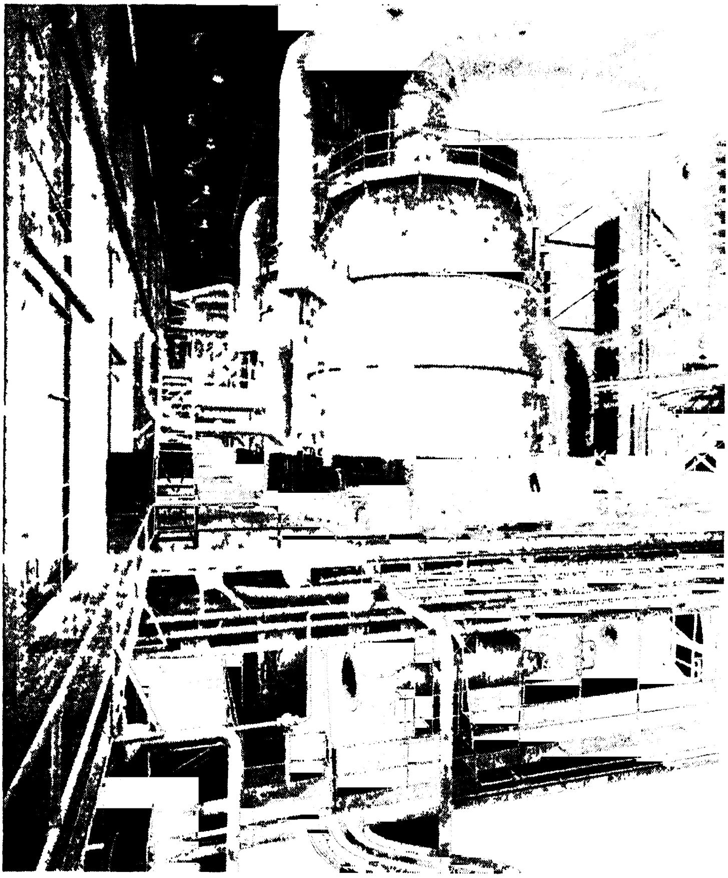

FIG. 4.—Vacuum evaporator unit at Trona, California Outside heaters are underneath pan (*Courtesy of American Potash and Chemical Corp*)

The process employed by the United States Potash Company[1] depends primarily upon the fact that sodium chloride is less soluble in a hot than in a cold saturated solution of potassium chloride. Thus, when a saturated solution of the mixed salts in water is cooled from its boiling point, KCl separates out contaminated with only what NaCl is entrained. The cold mother liquor is heated to 110°C. by use of heat exchangers employing exhaust steam, as shown in Fig. 5. The mother liquor is passed through the body of crushed salts contained in dissolvers with false bottoms. Potassium chloride goes into solution together with a small amount of sodium chloride. The enriched liquor is pumped to vacuum coolers and crystallizers. The vacuum is maintained by means of steam ejectors. After cooling to 27°C., the potassium chloride in suspension is pumped to settling tanks where a large part of the liquor is decanted through launders to be used again. The thickened crystal mass is filtered, washed, and dried on Oliver filters. The dried cake is crushed, screened, and conveyed either to warehouse or to cars.

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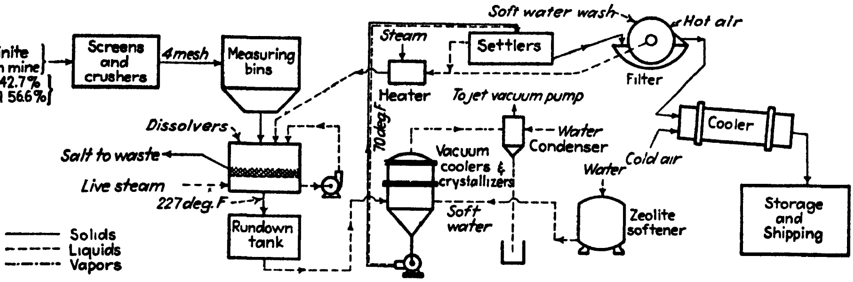
[1] CRAMER, Production of Potassium Chloride in New Mexico, *Ind. Eng. Chem*, **30**, 865 (1938).



Sylvinite	2.51 Tons	Per ton refined KCl
Water	40-50,000 Gal.	
Steam	2,500 Lb.	
Electricity	50 Kw-hr	
Direct labor	4-5 Man-hr	

FIG. 5—Potassium chloride from sylvinite.

The process of the Potash Company of America separates the KCl from the NaCl chiefly by a metallurgical concentration method using a soap-flotation process and represents the first adaptation to water-soluble ores of the flotation principle so long familiar in the concentration of insoluble ores. "The sylvinite ore, having been coarsely crushed underground, is fed to a Symons cone intermediate crusher, which in turn discharges to a series of fine crushers close-circuited with the screens." The ore is then wet-ground by ball mills to 100 mesh. "The mill product, having been ground sufficiently to release the KCl and NaCl, is treated in two series of flotation cells to float off a NaCl concentrate and depress a KCl concentrate. The NaCl crystals are washed and separated from the solution by means of a Dorr thickener and a Moore filter and sent to waste while the KCl concentrate, together with KCl crystals recovered from various circulating solutions, is separated by a classifier into fine and coarse fractions. Recovery of fines is accomplished by a thickener and centrifuges.[1]"

The flotation process is used also by the International Minerals and Chemical Corporation in the refining of sylvinite to produce potassium chloride.[1] This company also produces potassium sulfate[2] from the mineral langbeinite, $K_2SO_4 \cdot 2MgSO_4$, by reacting with KCl to yield the sulfate and the by-product $MgCl_2$. This latter is of particular interest as a raw material for the production of metallic magnesium, potassium chloride, and sulfate of potash-magnesia.

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[1] KIRKPATRICK, *op. cit.* p. 491; MCGRAW, New Mexico Sylvinite, *Ind. Eng. Chem.*, 30, 861 (1938).

The German[3] and other European deposits of potash are very extensive and form the basis of important industries. In addition to the major refined potash chemicals, considerable tonnages of the crude salts are sold in the local markets.

POTASSIUM SULFATE

Prior to 1939, the German potash industry was the chief source of potassium sulfate for American chemical and fertilizer industries, although considerable tonnages were being produced in this country by the interaction of potassium chloride and sulfuric acid as a side product of salt cake manufacture. With the termination of European imports the production of the salt was undertaken on the larger scale by the American Potash and Chemical Corporation through the interaction of burkeite, $Na_2CO_3 \cdot 2Na_2SO_4$, with potassium chloride,[4] followed in turn by the successful recovery of this salt from langbeinite by the International Minerals and Chemical Corporation as mentioned above. In its agricultural use potassium sulfate is preferred for the tobacco crop of the Southeast and for the citrus crop of southern California.

POTASSIUM HYDROXIDE AND CARBONATE

These two chemicals are very closely related. Some years ago most of the potassium hydroxide was made from potassium carbonate by reaction with calcium hydroxide.

$$K_2CO_3 + Ca(OH)_2 \rightarrow 2KOH + CaCO_3$$

But recently the production of potassium hydroxide by electrolysis of potassium chloride solutions has led to the production of potassium carbonate from potassium hydroxide. The abundant supplies of refined potassium chloride now cheaply available, combined with low-cost electrical energy, indicates that this will continue to be the principal method of production for the future. But potassium carbonate can be manufactured by heating potassium chloride with magnesium carbonate and carbon dioxide producing mixed carbonates of potassium and magnesium. This mixture is heated, and insoluble magnesium carbonate is filtered from the potassium carbonate. Potassium carbonate can also be made in a manner similar to the Solvay process.

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[1] HUBBELL, Refining Operations in New Mexico's Newest Potash Plant, *Chem. & Met. Eng.*, **48**, No. 6, 79 (1941). Flow sheet and pictures are given.

[2] KIRKPATRICK, Sulfate of Potash Produced from Langbeinite, *Chem. & Met. Eng.*, **28**, No. 1, 77 (1941).

[3] LILLY, Potash Recovery in Germany (flow sheet), *Eng. Mining J.*, **133**, 74–77 (1932); ULLMANN, "Enzyklopaedie der technischen Chemie," 2d ed., Kaliindustrie, Vol. **6**, p. 324, Urban & Schwarzenberg, Berlin and Vienna, 1928–1932.

[4] ROBERTSON, *op. cit.*, p. 136.

About 50 per cent of all the caustic potash consumed in the United States[1] is used in the manufacture of potash soaps. The remainder enters into the manufacture of dyes, synthetic organic chemicals, fine chemicals, carbon dioxide adsorption and air liquefaction, the textile industry, and glass manufacture. The carbonate, like the caustic, is used mainly for soaps and chemicals and is the preferred source of potash in the glass industry.

POTASSIUM NITRATE

Potassium nitrate is made by the double decomposition reaction of sodium nitrate and potassium chloride.

$$NaNO_3 + KCl \rightarrow NaCl + KNO_3$$

A strong hot solution of the sodium nitrate is made and the solid potassium chloride dumped into the kettle. Upon heating, the KCl changes to NaCl, whereupon the hot KNO_3 solution is run through the NaCl crystals in the bottom of the kettle. A little water is added to prevent any further deposition of NaCl, and the solution is cooled. A good yield of potassium nitrate results.

Potassium nitrate is frequently referred to as essential in the manufacture of slow-burning black powder which is used in fuses and in the ignition of smokeless powder. Other uses are in the manufacture of pyrotechnics and glass.[2]

POTASSIUM ACID TARTRATE

At present this chemical is obtained as crude argols, deposited in wine vats. The pure salt is obtained from the argols by leaching and crystallizing. In 1937 over 12,000 tons of argols were imported. The main uses are as the acid ingredient of baking powder, for the preparation of tartaric acid, and in medicine.

MIXED FERTILIZERS

When a balance is struck showing the removal of plant food from our soils by the crops we eat or wear or employ as a raw material in our factories, the paramount importance of fertilizers becomes strikingly clear. In fertilizers, we add back to the soil either the materials removed by plants or those chemicals needed in native soils either to make them productive at all or more productive. The food and clothing of the nations at our present rate of production are dependent largely on the use of fertilizers. Table 1, pertaining to potash, illustrates typical withdrawals from our soils. Table 4, Chap. XX, presents the nitrogen balance for the United States and shows the heavy annual loss.

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[1] TURRENTINE, Potassium Salts as Chemical Raw Materials, *Ind. Eng. Chem.*, **30**, 889 (1938).

[2] FINN, Potash in the Glass Industry, *Ind. Eng. Chem.*, **30**, 891 (1938).

Man early discovered that the excreta of animal life are the food for plant life. Indeed, the Chinese have maintained the fertility of their soil for 5,000 years by the application of this principle. Even in the superaesthetic civilization of the United States we recognize the need and apply animal manure on a large scale to maintain a better plant yield from our soils.

TABLE 1.—POTASH REMOVED PER ACRE BY VARIOUS CROPS[a]

Crop	Yield per acre	Potash removed, lb. K_2O
Alfalfa	4 tons	178.4
Clover hay	2 tons	65.2
Corn	75 bu. (plus stalks)	82.8
Cotton	600 lb. lint (entire plant)	59.6
Oats	50 bu. (plus straw)	40.8
Potatoes	300 bu.	95.0
Rye	35 bu. (grain)	40.0
Soybeans	25 bu. (beans)	86.0
Sugar beets	10 tons	64.0
Tobacco	1,000 lb. leaves (plus stalks)	78.0
Wheat	30 bu. grain (plus straw)	25.2

[a] LODGE, Potash in the Fertilizer Industry, *Ind. Eng. Chem.*, **30**, 878 (1938).

In fertilizers there are three main chemicals and many minor ones that are needed by our crops. The three principal ones are nitrogen, N, phosphoric acid, P_2O_5, and potash, K_2O. We generally speak of fertilizers as having formulas, such as 10-6-4, 2-12-6, or 0-12-15, which mean that these fertilizers have 10, 6, 4, or 2, 12, 6, or 0, 12, 15 per cent, respectively, of total nitrogen, N, of available phosphate, P_2O_5, and of soluble potash, K_2O. Note, for a memory jog, that these constituents are in alphabetical order. Another way of evaluating these fertilizer formulas is as "units." Here one unit is 1 per cent of a ton or 20 lb. Hence the first of the formulas given above would contain 10 units of nitrogen, 6 units of P_2O_5, and 4 units of K_2O. In addition, many of the commercial fertilizers contain the minor chemicals needed by plants. Table 2 gives a summary of the important chemicals that are commercially used to supply these three fertilizing radicals. All these constituents are mechanically mixed together to give a uniform product and this composition checked by careful analysis. A rotating elongated cylinder is frequently employed for the mixer.

Not all chemicals or other constituents of fertilizers are available to all plants with equal facility because so much depends upon the nature of the chemical used, upon the other materials in the soil, and in particular on the soil pH or its chemical reaction as well as upon the crop itself. From this it can be seen that not only must the mixing but also the application of the fertilizers be carried out properly. Fortunately the farmers of the nation have at their call the various county agents of the Department of Agriculture who act in cooperation with various experimental stations and can select and supply that fertilizer which will give the best results for the dollar expended.

TABLE 2.—FERTILIZERS AND FERTILIZER MATERIAL USED IN THE UNITED STATES[a]

Production of Fertilizers in 1939

	Short Tons
Complete fertilizers	5,088,468
Superphosphates including concentrated phosphates	2,757,340
Other fertilizers	695,221

Fertilizer Materials (per fertilizer year)

	1939–1940 (short tons)	1940–1941 (short tons)
Sulfate of ammonia	513,000	567,000
Nitrate of soda	748,000	783,000
By-product ammonia liquor	35,000	35,000
Synthetic N-containing solutions	85,000	101,000
Cyanamide	138,000	124,000
Calcium nitrate and urea fertilizers	88,000	43,000
Ammonium phosphates	67,000	48,000
Nitrate of potash, nitrate of soda-potash	46,000	22,000
Other potash materials	770,000	790,000
Cottonseed meal	135,000	160,000
Other natural organic fertilizer materials	660,000	650,000
Bulk superphosphate	3,355,000	3,400,000
Basic slag	35,000	40,000
Bones and bone meal	92,000	90,000
Ground phosphate rock	140,000	140,000

[a] *Chem. & Met. Eng.*, **48**, No. 2, 95 (1941); *Chem. & Met. Eng.*, **49**, No. 2, 87 (1942); 1940 Census of Manufactures.

As many of the constituents necessary for fertilizers must be shipped a considerable distance, the trend in recent years has been to use the more concentrated constituents for fertilizers.[1] In a 10-6-4 mixture there is a total of only 20 per cent of active fertilizer constituents. The other 80 per cent consists of filler, carrier, or soil-conditioning materials. The day will come everywhere, as the day has come in many places, when much more concentrated fertilizers are economically available to the farmers. If necessary, the diluting materials can be added from the farmers' own back yards to prevent a too strong or a burning action on the delicate young plants. Examples of concentrated fertilizer chemicals are ammonium nitrate, potassium metaphosphate, ammonium phosphate, and potassium nitrate. The production of these at competitive prices is the only thing that keeps them from being used more extensively.

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[1] MERZ, New Fertilizer Materials, *U.S. Dept. Agr., Circ.* 185, 1940.

Minor constituents that research has shown to be necessary for plant life are sodium, calcium, and magnesium compounds in small amounts accompanied by much smaller quantities of boron, iron, sulfur, manganese, zinc, and copper compounds. Some of these derivatives, such as boron, are disadvantageous if their presence is larger than a certain minimum. Everyone knows that water and carbon dioxide are consumed by the plants in enormous amount and that humus is helpful to better the general soil condition.

The modern fertilizer chemist in cooperation with the soil scientist actually feeds the plants and overcomes much of the necessity of letting the fields regenerate their fertility by lying fallow every third season as was the custom from ancient times. To be sure, the modern soil scientist also utilizes certain crops to replenish some aspects of soil fertility, as is done so extensively to supply nitrogen by the use of legumes such as clover and alfalfa.

Nitrogen Fertilizing Constituents.—Chapter XX presents the source and methods of manufacture of various nitrogen compounds which are used both in industry and fertilizers. Tables 2 and 3 indicate that nitrogen is employed in the form of ammonium salts, nitrates, and organic nitrogenous materials. Nitrogen compounds stimulate the

TABLE 3.—PRINCIPAL FERTILIZER CONSTITUENTS

Containing Nitrogen, N:
- Nitrates of ammonium, sodium, calcium and potassium
- Ammonium salts, as sulfate, phosphate, chloride, and nitrate
- Ammonia for ammoniating superphosphates
- Calcium cyanamide
- Soluble organic products: urea and urea solution in liquid ammonia
- Insoluble organic: cottonseed meal, tankage, fish scrap, sewage sludge, guano

Containing Phosphoric Acid, as P_2O_5:
- Superphosphate
- Ground phosphate rock
- Bone meal
- Basic slag

Containing Potash, as K_2O:
- Potassium chloride, pure and crude mixtures (manure salts)
- Potassium sulfate, nitrate, and carbonate (crude)

vegetative growth in plants. Nitrogen-containing compounds are an essential part of all protoplasm through the agency of which chemical changes take place in the cells. Plants lacking nitrogen have yellow leaves. Too much nitrogen causes rank growth and delays maturity.

Phosphate Fertilizing Constituents.—Throughout the world there exist very large deposits of apatite or phosphate rock. This has the formula, $3Ca_3(PO_4)_2{\cdot}CaF_2$, from which it can be seen that this compound is really calcium fluorphosphate. If simply placed on the soil after being very finely ground, it becomes gradually available. As Table 2 shows, over 140,000 tons are consumed yearly. If, however, this phosphate rock is decomposed by the action of sulfuric acid, superphosphate results in which 18 to 20 per cent of P_2O_5 is immediately available. Superphosphate manufacture is described in Chap. XVIII. To save some cost in transporting and to secure a more concentrated fertilizer, the phosphate rock is decomposed with phosphoric acid, yielding a stronger fertilizer known as *triple superphosphate*, which contains 48 per cent P_2O_5. Bone meal, made by grinding old or fresh bones, is also an important source of this fertilizing constituent. Indeed, it is known that many years after the herds of buffaloes were slaughtered for their hides, their whitened bones were collected from the plains of the West for their fertilizer value. The function of phosphorus in plants is really complex, the phosphates stimulating plant growth, causing resistance to disease, producing more vigorous seedlings, and hastening crop maturing. Phosphorus like nitrogen is a part of protoplasm that is essential to life.[1]

Potash Fertilizing Constituents.—For three quarters of a century, the rich deposits of Germany satisfied the potash demands of the world. However, the uncertain supplies in wartime forced the United States and other nations to develop their own potash resources to ensure the productivity of their soils. Potassium chloride or muriate of potash, either as an almost pure salt or in the form of impure manure salt, is widely used in fertilizer mixes. On certain crops, as, for instance, tobacco, the chloride ion in high concentration is disadvantageous; consequently potassium sulfate or potassium nitrate, when available, is preferred. When fields lie fallow, and even in the process of ordinary weathering, potassium minerals such as feldspar gradually decompose, liberating from year to year considerable amounts of potash to the plants. Some of the potash absorbed by the plant remains in the vegetative parts which are not normally sold off the farm. Potassium is an essential element in all growing plants and in particular in all crops; it is necessary in all cell metabolic processes. Lodge[1] summarizes the effect of potash on plants by writing,

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[1] Van Slyke, "Fertilizers and Crops," Orange Judd Publishing Co., Inc., New York, 1914.

> (*a*) It facilitates either the production or the translocation of sugars and starches from the leaf, hence its value for sugar- and starch-making crops; (*b*) it stiffens the straw of cereal crops and the grass tribe generally; and (*c*) it enables the plant to withstand adverse conditions of soil, climate, and disease, making it more resistant to drought, rust, and other diseases. By balancing the plant food ration, potash tends to counteract rankness of growth developed by abundant nitrogen.

Problems

1. Five hundred metric tons of fixed nitrogen are needed. Assuming 95 per cent purity, what weight of urea should be ordered? Assuming 95 per cent purity, repeat the calculations for ammonium sulfate and Chilean nitrate. (One metric ton = 2,205 lb.)

2. A fertilizer is to have a 2-16-4 ratio and is to be made from KNO_3 and a Peruvian guano which contains 1.95 per cent N_2, 19 per cent P_2O_5, and $3\frac{1}{3}$ per cent K_2O. Calculate the amounts of each per ton of fertilizer.

3. It is desired to make a 4-14-2 fertilizer by mixing ammonium dihydrogen phosphate and ammonia with a 2-11-3 fertilizer already on hand. How much of each of these three materials will be necessary to make 100 lb. of the 4-14-2 fertilizer? Is a filler necessary? If so, how much?

4. Make a fertilizer with the composition:

N_2	4 per cent
P_2O_5	8 per cent
K_2O	10 per cent

from

a. $NaNO_3$ containing 16 per cent N_2.
b. Acid phosphate containing 15 per cent available P_2O_5.
c. KCl containing 50 per cent K_2O.
d. Inert filler.

How many pounds of each of these materials will be required per ton of fertilizer?

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[1] LODGE, Potash in the Fertilizer Industry, *Ind. Eng. Chem.*, **30**, 878 (1938); TRUOG and JONES, Fate of Soluble Potash Applied to Soils, *Ind. Eng. Chem.*, **30**, 882 (1938); HOFFER, Potash in Plant Metabolism, *Ind. Eng. Chem.*, **30**, 885 (1938); also Symposium—Potash in Agriculture, *Soil Sci.*, **55**, 87*ff.* (1943).

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CHAPTER XIV

SALT AND MISCELLANEOUS SODIUM COMPOUNDS

There are a considerable number of sodium salts that are of definite industrial necessity. Most of these are derived directly or indirectly from ordinary salt so far as their sodium content is concerned. In one sense, the sodium may be viewed simply as a carrier for the more active anion to which the compound owes its industrial importance. For instance, in sodium sulfide it is the sulfide part that is the more active. Similarly this is the case with sodium thiosulfate and sodium silicate. We could use in most cases the corresponding potassium salts which in past years were consumed more extensively. The present situation is that sodium salts can be manufactured more cheaply and in sufficient purity to meet the industrial demands. Therefore, industry has turned, in the last few decades, to a greater utilization of the various sodium salts. Sodium salts are described elsewhere as follows: Sodium chlorate and perchlorate in Chap. XVI; sodium hypochlorite in Chap. XV, which includes the various sodium alkali compounds; the sodium phosphates are in Chap. XVIII; sodium nitrate in Chap. XX; and sodium bichromate and sodium borate are in the miscellaneous inorganic Chap. XXI.

SODIUM CHLORIDE OR COMMON SALT

Historical.—Salt has long been an essential part of the human diet. It has served as an object of worship and as a medium of exchange, lumps of salt being used in Tibet and Mongolia for money. Its distribution has been employed as a political weapon by ancient governments and even today in Oriental countries high taxes are placed on salt.

Uses and Economics.—Sodium chloride is the basic raw material of a great many chemical compounds such as sodium hydroxide, sodium carbonate, sodium sulfate, hydrochloric acid, sodium phosphates, and sodium chlorate and chlorite.[1] It should be remembered also that it is the source of many other compounds through its derivatives. Practically all chlorine comes from the electrolysis of sodium chloride. It is important in the zeolite process of water softening, and it has many uses in the field of organic chemistry such as the salting out of soap and the precipitation of dyes. It is employed to preserve fish, meat, and hides both directly and indirectly through the medium of refrigeration. The dairying and pickling industries also consume large quantities of sodium chloride. Probably the most important use of sodium chloride is as an essential part of everyone's diet. Large quantities of the purest of sodium chloride are sold as table salt. The latter may have a small amount of iodide added in certain sections of the country.

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[1] Looker, Salt as a Chemical Raw Material, *Chem. Industries*, **49**, 594–601, 790–799 (1941).

The total salt output in the United States in 1942, including evaporated salt brine and rock salt, amounted to 13,693,284 tons valued at $38,144,234.[1] In 1942, 86 plants were in operation, 66 plants produced evaporated salt, 20 produced rock salt, and 11 produced all the salt brine for consumption.

TABLE 1.—PRODUCTION AND VALUE OF SODIUM SALTS MANUFACTURED IN THE UNITED STATES IN 1939[a]

Salt	Production, tons	Value
Sodium chloride	10,003,500	$26,118,100
Sodium sulfate	224,749	2,291,940
Glauber's salt	34,493	539,770
Niter cake	34,100	607,280
Sodium sulfite	11,210	693,770
Sodium hydrosulfite	11,723	3,576,660
Sodium sulfide (60–62 per cent)	31,480	1,633,900
Sodium thiosulfate	25,710	1,142,100
Sodium phosphates, dibasic	13,630	1,207,300
Sodium phosphates, tribasic	114,690	4,819,800
Sodium phosphates, pyro	42,210	4,200,000

[a] *Chem. & Met. Eng.*, **48**, No. 2, 115 (1941), or "Minerals Yearbook" for 1940.

Manufacture.—Salt occurs throughout the United States and is obtained in three different ways. One of these methods is by solar evaporation of sea water or salt lake water, or by evaporation and crystallization from brines pumped from wells. The second method is the mining of rock salt while the third involves the direct consumption of the salt brine. About 500,000 tons are produced annually by solar evaporation, a large portion of which comes from the San Francisco Bay region and the Great Salt Lake of Utah.[2] The purity of salt first obtained from the evaporation of salt water is usually about 95 per cent; salt that is mined varies very widely in composition depending on the locality in which it is found. Some rock salt, however, runs as high as 99.5 per cent pure sodium chloride. The solution obtained from wells is usually only about 98 per cent pure.

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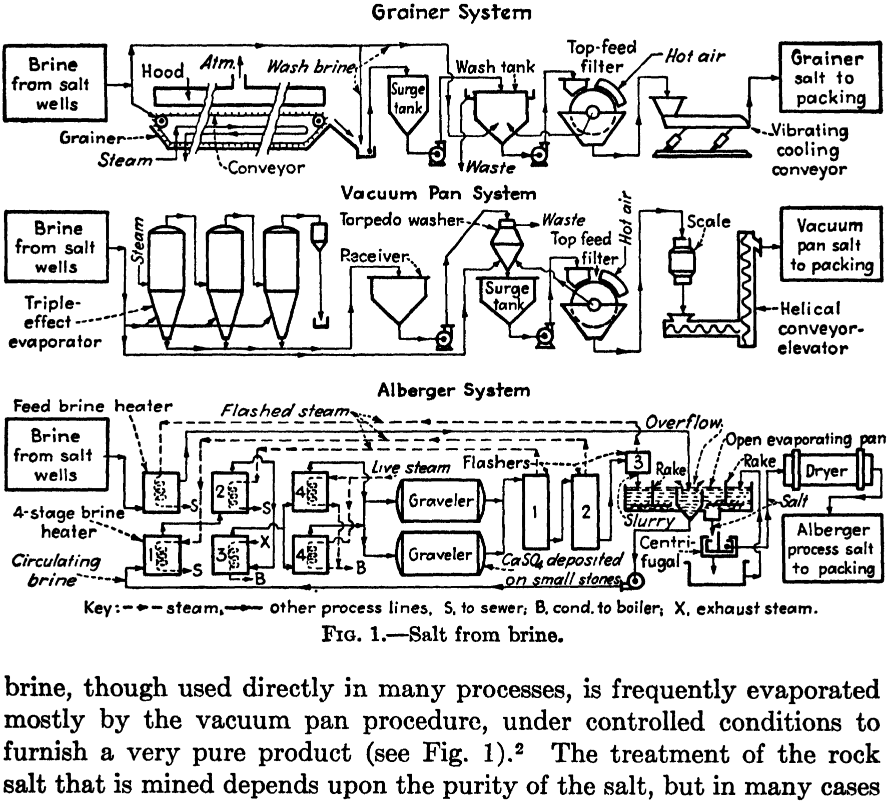
[1] *U.S. Bur. Mines M.M.S.* 1082.

[2] BUCHEN, Evaporating Salt from the World's Largest Mineral Deposits, *Mining and Met.*, **18**, 335 (1937).

For many purposes the salt obtained from the mines and by direct evaporation of salt solutions is pure enough for use; however, a large portion must be purified. If the evaporated salt from brines is to be treated, the solid may be dried in a kiln at 300°F. and the principal impurity, Glauber's salt, dehydrated and blown up by the air blast in the drier.[1] The only other treatment given this salt is crushing and screening. A purity of 99.8 per cent is easily obtained. Artificial brine, though used directly in many processes, is frequently evaporated mostly by the vacuum pan procedure, under controlled conditions to furnish a very pure product (see Fig. 1).[2] The treatment of the rock salt that is mined depends upon the purity of the salt, but in many cases it is sufficiently high grade for direct use.



Key: –►– steam, —►— other process lines, S, to sewer; B, cond. to boiler; X, exhaust steam.

Fig. 1.—Salt from brine.

The *caking* of salt crystals is very troublesome and can be minimized as pointed out by Perry[3] if the following conditions are maintained:

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[1] Brighton and Dice, Increasing the Purity of Common Salt, *Ind. Eng. Chem.*, **23**, 336 (1931).

[2] For a detailed description of the purification and manufacture of salt see Badger and Baker, "Inorganic Chemical Technology," Chap. 2, 2d ed., McGraw-Hill Book Company, Inc., New York, 1941; Perry, *op. cit.*, p. 1590; Phalen, "Technology of Salt Making in the United States," *U.S. Bur. Mines Bull.* 46, p. 41. See also Chap. 9 by MacMullin in "Rogers' Manual of Industrial Chemistry," 6th ed., D. Van Nostrand Company, Inc., New York, 1942.

[3] Perry, *op. cit.*, p. 1799. Critical humidity defined.

1. Highest possible critical humidity is increased in case of salt by the removal of such impurities as calcium chloride, magnesium chloride, or free acid, all of which have a lower critical humidity than pure sodium chloride.
2. Most uniform graining which brings about the greatest percentage of voids for the size of crystals desired and the least points of contact.
3. Coating with a powder capable of absorbing some moisture. For salt magnesia or tricalcium phosphate is employed.

SODIUM SULFATE (Salt Cake and Glauber's Salt)

Hydrochloric acid is related to nitric acid in the sense that niter cake was often used as a raw material with salt to produce hydrochloric acid. Now sulfuric acid is reacted directly on the salt (see Chap. XXI). The other product of this reaction is salt cake or crude sodium sulfate. This crude salt cake usually contains impurities of iron, calcium, magnesium compounds, and salt with sulfuric acid. Glauber's salt, $Na_2SO_4 \cdot 10H_2O$, is made by purifying and crystallizing the crude salt cake. Anhydrous sodium sulfate and Glauber's salt also occur naturally in many places.[1]

Uses and Economics.—The principal consumptions of this compound are as a source of alkali for the manufacture of sulfate pulp and for the production of sodium sulfide. Other important uses are in the manufacture of glass, Glauber's salt, sodium silicate, sodium hyposulfite, nickel smelting, barium sulfate, sodium aluminum sulfate, hog and cattle powders, and in dyeing.

The sales of salt cake from chemical works as well as from natural sources amounted to 224,749 short tons in 1939, valued at $2,291,940; 34,493 tons of Glauber's salt were sold in 1939 valued at $539,770.[2]

Manufacture of Salt Cake.—The equations for the production of salt cake are[3]

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$
$$NaHSO_4 + NaCl = Na_2SO_4 + HCl$$

The equipment and the procedure for commercializing these reactions are described under Hydrochloric Acid in Chap. XXI. When the temperature has reached the proper level in the furnace, the finely ground salt and other raw material are charged. The furnace runs continuously, batch after batch, until shut down for the necessary periodical cleaning and repair. Most products from the Mannheim furnace go into the manufacture of other materials in the same plant where this type of furnace is operated.

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[1] MANNING, Chemicals from California's Desert, *Chem. & Met. Eng.*, **48**, No. 9, 96 (1941).

[2] Table 1.

[3] LAURY, "Hydrochloric Acid and Sodium Sulfate," Reinhold Publishing Corporation, New York, 1927.

Another method of making sodium sulfate, which originated in Europe, is the Hargreaves process. The equation for the reaction is as follows:

$$4NaCl + 2SO_2 + 2H_2O + O_2 = 2Na_2SO_4 + 4HCl$$

This is carried out by passing sulfur dioxide and air from a furnace over prepared salt lumps in vertical steel chambers with false bottoms. Several of these chambers are run in series, and the gas is moved countercurrently. The complete cycle for the reaction, cleaning, and repacking is three days for each individual chamber. Very good cake and hydrochloric acid were made in this process, but the fact that it requires a large amount of hand labor has prohibited its wide use in this country. The Bay Chemical Co. of Weeks Island, La., is the only American Hargreaves plant.

Because of the increased demand for sodium sulfate in the kraft-paper manufacture, "synthetic salt cake" has become an important product. Synthetic salt cake is a sintered mixture of soda ash and sulfur in the proportions of 3 parts of sulfur to 10 of soda ash. This product[1] is not satisfactory as a substitute for sodium sulfate in applications other than the kraft paper industry. In 1940, 400 tons per day were being produced.

$$Na_2CO_3 + S + 1\tfrac{1}{2}O_2 \rightarrow Na_2SO_4 + CO_2; \qquad \Delta H = -1950 \text{ B.t.u. per lb.}^1$$

Manufacture of Glauber's Salt.—Glauber's salt is made by dissolving salt cake in mother liquor, removing the impurities, clarifying, and crystallizing. The salt cake is dissolved in large, circular, lead-lined wooden tanks. The solution is then treated with a paste of chloride of lime followed by milk of lime in sufficient quantities to neutralize the solution. Stirring is carried out by a paddle and heating by a lead pipe running to the bottom. The precipitated impurities of iron, magnesium, and calcium are allowed to settle, and the clear solution is run to crystallizers by side outlets. The precipitated mud is washed with water and the water is used as make-up for the process. Crystallization is carried out in pans lined with lead. When the solution cools to room temperature, the pan is drained and the crystals are collected and centrifuged.

Pure *anhydrous sodium sulfate* is also sold in the market. It is made by dehydrating Glauber's salt in a brick-lined rotary furnace, by crystallizing out from a hot concentrated solution, or by chilling and dehydrating.[2] Figure 2 shows the steps in the production of anhydrous sodium sulfate from naturally occurring Glauber's salt. With the increasing consumption of sodium sulfate by the expanding kraft paper industry, the development of sodium sulfate from these natural sources has been much stimulated.

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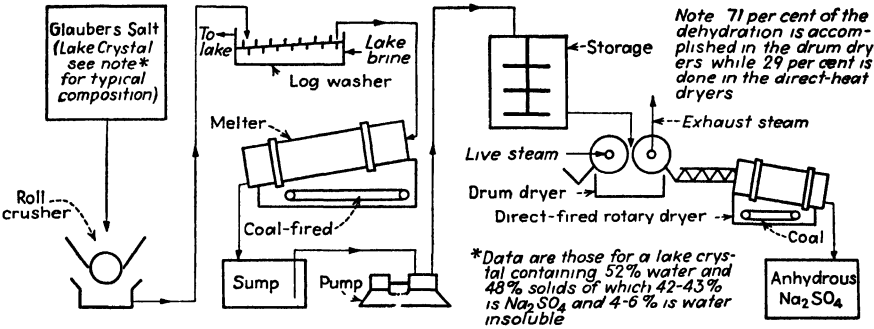
[1] SOVELL, The Application of Synthetic Salt Cake, *Paper Trade J.*, Aug. 22, 1940; SOVELL, New Ideas on the Use of Salt Cake in Kraft Pulp Process, *Paper Mill*, Dec. 9, 1939.

[2] DOUGLAS and ANDERSON, Submerged Combustion as Applied to Sodium Sulfate Production, *Chem. & Met. Eng.*, **48**, No. 5, 135 (1941).



Note 71 per cent of the dehydration is accomplished in the drum dryers while 29 per cent is done in the direct-heat dryers

*Data are those for a lake crystal containing 52% water and 48% solids of which 42-43% is Na_2SO_4 and 4-6% is water insoluble

Based on article by J B Pierce. Chem & Met, Dec 1937, P 718

Lake crystal*	5 000 lb	Per ton anhyd Sodium sulphate (95+%) produced
Coal (6 800 B t u lignite)	415 lb	
Steam (not dupl of coal)	3 650 lb	
Total power (incl mining)	37½ kw-hr	

FIG. 2.—Flow sheet for naturally occurring sodium sulfate by the three-stage procedure.

SODIUM BISULFATE OR NITER CAKE

Sodium bisulfate, $NaHSO_4$, is commonly called *niter cake* because it was obtained by the now almost obsolete reaction of sodium nitrate or "niter" with sulfuric acid.

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$

The acid sodium sulfate may be manufactured from salt and sulfuric acid. This compound is used as a mild acid ingredient in dye baths, in the cleaning of sanitary porcelain objects, and as a cleaner in automobile radiators. It is also employed as a flux in metallurgical industries.

SODIUM BISULFITE

Uses and Economics.—Sodium bisulfite finds industrial employment either in solution or as a solid. The solid is of the anhydrous form and has the formula $NaHSO_3$ for the pure reagent. The commercial product usually consists almost entirely of $Na_2S_2O_5$ known as *sodium pyrosulfite* or *sodium metabisulfite*, which is the dehydrated derivative of two molecules of sodium bisulfite. The solutions may be easily shipped, stored, and handled in lead-lined equipment. In the tanning industry this acid salt is used as a reducing agent for chrome solutions; in the textile field it is a bleaching agent, an antichlor, and a raw material for the manufacture of hydrosulfite solutions. It is also consumed in the paper, photographic, and organic chemical industries.

Manufacture.—Sodium bisulfite is produced by passing sulfur dioxide through a solution of mother liquors from previous processes containing in solution small amounts of sodium bisulfite and in suspension a considerable amount of soda ash. The reaction taking place is

$$2NaHSO_3 + \underline{2Na_2CO_3} + 2H_2O + 4SO_2 \rightarrow \underline{6NaHSO_3} + 2CO_2$$

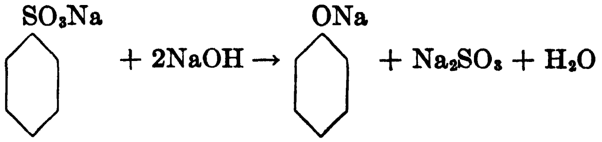
The product is obtained as a *suspension* which is removed from the solution by centrifuging. The dried product is really the sodium metabisulfite, $Na_2S_2O_5$.

SODIUM SULFITE

Uses and Economics.—Sodium sulfite is a compound that is very easily oxidized. For this reason it is employed in many cases where a gentle reducing agent is desired. It is employed to bleach wool and silk, as an antichlor after the bleaching of yarns, textiles, and paper, as a preservative for foodstuffs, and to prevent raw sugar solutions from coloring upon evaporation. It is very widely used in the preparation of photographic developers as a preventive of the oxidation of hydroquinone and other agents. It has a small application in the field of medicine as an antiseptic and as an antizymotic for internal use. The reason for the increase in the use of sodium sulfite is the recent discovery that its addition to boiler feed water will remove oxygen from the water and thus help prevent corrosion and scale formation. Any excess of this salt is sold to the sulfate pulp mills.

Manufacture.—The most important commercial procedure for this compound is by passing sulfur dioxide into a solution of soda ash until the product has an acid reaction. At this point the solution consists chiefly of sodium bisulfite. This may be converted into sodium sulfite by adding more soda ash to the solution and boiling until all the carbon dioxide is evolved. The reaction is carried out in large lead-lined wooden vessels. After the solution has settled, it is concentrated, whereupon crystals of $Na_2SO_3 \cdot 7H_2O$ settle out upon cooling.

Another commercial source of this compound in the crude anhydrous form is from the preparation of phenol by the fusion of sodium benzene sulfonate with sodium hydroxide.[1]



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[1] Groggins, "Unit Processes in Organic Synthesis," 2d ed., p. 628, McGraw-Hill Book Company, Inc., New York, 1938.

SODIUM HYDROSULFITE[1]

One of the most important chemicals in the dyeing and printing industries is sodium hydrosulfite. It is a very powerful reducing agent with a specific action on many dyes, particularly the "vat dyes," reducing them to the soluble form. This reducing agent is employed for stripping certain dyes from fabrics and for bleaching straws and soaps. Formerly one of the main difficulties with this compound was the lack of stability; however, this has been corrected and it may be shipped and stored. Another name for this substance is *sodium hyposulfite,* though the dyehouse workers call it simply *hydro.*

Manufacture.—There are two methods of manufacture both of which require zinc dust. In the first process the zinc dust is allowed to reduce sodium bisulfite at room temperature:[2]

$$2NaHSO_3 + H_2SO_3 + Zn \rightarrow ZnSO_3 + Na_2S_2O_4 + 2H_2O$$

The products of the reaction are treated with milk of lime to neutralize any free acid and hence to reduce the solubility of the $ZnSO_3$ which is filtered off. Sodium chloride is added to salt out the $Na_2S_2O_4 \cdot 2H_2O$. This is dehydrated with alcohol and dried. The crystals are stable only in the dry state.

The second process consists of treating an aqueous suspension of zinc dust in formaldehyde with sulfur dioxide at 80°C. A double decomposition reaction is carried out with soda ash forming the sodium salt. A pure product is obtained by evaporation in vacuum.

SODIUM SULFIDE

Uses and Economics.—Sodium sulfide, Na_2S, is an inorganic chemical that has attained a very important position in the organic chemical industry. It is consumed as a reducing agent in the manufacture of amino compounds, and it enters into the preparation of many dyes. It is also employed extensively in the leather industry as a depilatory, *i.e.,* for the removal of hair from hides. Sodium polysulfide is one of the necessary reactants for making Thiokol synthetic rubber. Other industries where its use is important are the rayon, metallurgical, photographic, and engraving fields. The production of sodium sulfide in 1939 was 31,480 tons based on 60 to 62 per cent Na_2S and valued at $1,633,900.

Manufacture.—This chemical may be obtained as 80 per cent crystals or as 62 per cent flakes. Here the percentage refers to Na_2S. Solutions of it may be shipped in steel very conveniently. One disadvantageous property of sodium sulfide is its deliquescence. It crystallizes with nine molecules of water, $Na_2S \cdot 9H_2O$.

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[1] This compound is named *sodium hyposulfite* by *Chemical Abstracts.* In commerce it is also called *sodium sulfoxylate.*

[2] RANSHAW, Hydrosulfites and Their Derivatives, *Chem. Age,* **41,** 359 (1939); PRATT, Sodium Hydrosulfite as a Dry Powder, *Chem. & Met. Eng.,* **31,** 11 (1924).

There are three methods of producing this chemical. The oldest and probably the most used is the reduction of sodium sulfate with powdered coal in a reverberatory furnace. Another similar process is the reduction of barite in the same manner, leaching, and double decomposition with soda ash. The third and newest method of production involves the saturation of a caustic soda solution with hydrogen sulfide and the addition of another equal portion of sodium hydroxide. For the reactions involving the reduction of salt cake

$$Na_2SO_4 + 4C \rightarrow Na_2S + 4CO$$
$$Na_2SO_4 + 4CO \rightarrow Na_2S + 4CO_2$$

very drastic conditions are needed. Since the reaction must be carried out above 850°C., there has been a great deal of work undertaken to improve not only the medium in which the reaction is carried out but also the conditions for the reaction so that lower temperatures may be used.[1] Specially designed small reverberatory furnaces seem to give the least difficulty because they avoid overheating the charge. The reaction takes place in a liquid phase and is very rapid. Rotary kilns of the type used for calcining limestone have been applied with some success to this reaction. The reduction of barium sulfate takes place very similarly.

The substance issuing from the furnace is known as *black ash*. This product is run into iron tanks and allowed to cool. It may be used in this crude form but it contains many impurities. This crude sulfide may be dissolved hot; after settling, it may be run into shallow crystallizing tanks where colorless crystals of $Na_2S \cdot 9H_2O$ separate out. A more concentrated sulfide may be obtained by evaporating the liquor at 160°C. for 4 to 6 hr. in a cast-iron pot. The molten hot sulfide is then pumped into ordinary caustic soda steel drums for shipping.

SODIUM THIOSULFATE

Sodium thiosulfate crystallizes in large, transparent, extremely soluble prisms with five molecules of water. It is used as a mild reducing agent like sodium sulfite. It is employed as an antichlor following the bleaching of cellulose products and as a source of sulfur dioxide in the bleaching of wool, oil, and ivory. In photography it is used to dissolve unaltered silver halogen compounds from negatives or prints where it is commonly called *hypo*. It is a preservative against fermentation in dyeing industries and serves in the preparation of mordants. Other minor uses of sodium thiosulfate are in the reduction of indigo, in the preparation of cinnabar, in the preparation of silvering solutions, and in medicine.

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[1] WHITE and WHITE, Manufacture of Sodium Sulfide, *Ind. Eng. Chem.*, **28**, 244 (1936).

Manufacture.—There are several methods for the production of sodium thiosulfate, the most important of which is from sodium sulfite and free sulfur.

$$Na_2SO_3 + S \rightarrow Na_2S_2O_3$$

The reaction of the sulfur with a concentrated solution of sodium sulfite is carried out in a ceramic-lined iron pot provided with agitation. The resulting liquor is concentrated and crystallized. The crystals formed, $Na_2S_2O_3 \cdot 5H_2O$, should be packed immediately in airtight containers to prevent efflorescence.

A second method of preparation is from sodium sulfide. Sulfur dioxide is passed into a solution of sodium sulfide and sodium carbonate of low concentration (not more than 10 per cent of each).

$$Na_2CO_3 + 2Na_2S + 4SO_2 \rightarrow 3Na_2S_2O_3 + CO_2$$

The sodium thiosulfate is obtained by evaporation and crystallization.

SODIUM NITRITE

From the standpoint of the dye industry, sodium nitrite is a very important chemical. Here it is employed for the diazotization of amines for making azo dyes. It does not have a great many other uses. Formerly, it was prepared by the reaction,

$$NaNO_3 + Pb \rightarrow NaNO_2 + PbO$$

Sodium nitrite is now manufactured by passing the oxidation product of ammonia into soda ash solution.

$$Na_2CO_3 + 2NO + \tfrac{1}{2}O_2 \rightarrow 2NaNO_2 + CO_2$$

Any sodium nitrate also formed may be separated by crystallization. Lead-lined equipment is satisfactory.

SODIUM SILICATES

Uses and Economics.—Sodium silicates are unique in that the ratio of their constituent parts, Na_2O and SiO_2, may be varied to obtain the desired properties. Silicates that have a ratio from $1Na_2O/1.6SiO_2$ up to $1Na_2O/4SiO_2$ are called *colloidal* silicates. Sodium metasilicate has a ratio of 1 mole of sodium oxide to 1 mole of silica, Na_2SiO_3. A compound with a higher content of sodium oxide with $1\frac{1}{2}$ moles of Na_2O to 1 mole of SiO_2 is called *sesquisilicate.* Another compound still higher in sodium oxide content is sodium orthosilicate, Na_4SiO_4, which contains 2 moles of Na_2O to 1 mole of SiO_2.

The lower colloidal silicates are sold as 20 to 50 per cent solutions called *water glass*. They are used for fireproofing, for adhesives, for making ceramic glazes, as a builder in soaps, as detergents, as sizings, for the preservation of eggs, and in a large number of other uses.[1] The sodium metasilicate exists in the hydrated form and is sold as a solid. It is more alkaline than soda ash and is used in metal cleaning and as a strongly alkaline detergent. Sodium sesquisilicate, $Na_4SiO_4 \cdot Na_2SiO_3 \cdot 11H_2O$, and sodium orthosilicate, Na_4SiO_4, are employed in the same fields as the metasilicates but where a more strongly alkaline product is needed. The metasilicates are used in the kier boiling of cotton and in bleaching in the textile industries in conjunction with peroxides.

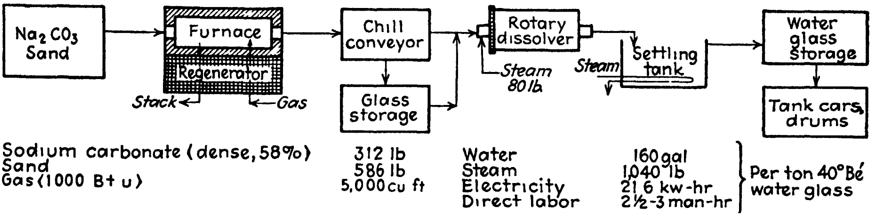

Fig. 3.—Flow sheet for manufacture of sodium silicate.

Manufacture.—In general the silicates may be obtained by fusing sodium carbonate and silica (sand) in a furnace resembling that for the manufacture of glass as shown in Fig. 3. The product is run off from the furnace and solidified. It is broken up and ground by suitable machinery. If the material is to be sold as a solution, it is dissolved in water under pressure in a rotary dissolver. The resulting solution may be adjusted to 40°Bé.

SODIUM PEROXIDE

Sodium peroxide is a pale-yellow hydroscopic powder. It absorbs moisture from the air and forms a snow-white hydrate, $Na_2O_2 \cdot 8H_2O$. When added to water, this compound forms sodium hydroxide and oxygen. It is a powerful oxidizing agent, and its principal uses depend upon this property. It is employed for the bleaching of wool, silk, and fine cotton articles and in chemical synthesis.

Manufacture.—It is prepared by burning sodium in an excess of air. The reaction is carried out in heated revolving drums or continuously by placing sodium in wagons and moving them through a furnace maintained at 300°C. A current of dry air is passed through the furnace countercurrent to the wagons containing the sodium. The product has a purity of about 95 per cent. Sodium peroxide must be packed in clean dry iron or nickel. Care should be taken in handling since, when it is placed on paper or wood, the heat of hydration of the material is sufficient to cause ignition. Fused sodium peroxide reacts with platinum, iron, copper, tin, and brass but not with nickel.

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[1] Stericker, Some Uses of Sodium Silicates in the Textile Industry, *Am. Dyestuff Reptr.*, **27**, 274 (1940); Jeglum, The Properties of Soluble Silicates, *Chem. Industries*, **49**, 604 (1942).

SODIUM PERBORATE

Sodium perborate,[1] $NaBO_3 \cdot 4H_2O$, is a mild oxidizing agent that has recently gained widespread use in the medical and dental fields. It is recommended as a mouthwash because of its oxidizing and cleansing effects. Other uses are as oxidizing and bleaching agents in cosmetics, soaps, and textiles. It is made by mixing solutions of borax, sodium peroxide, and hydrogen peroxide, heating slightly, and allowing to crystallize.

$$Na_2B_4O_7 + Na_2O_2 + 3H_2O_2 \rightarrow 4NaBO_3 + 3H_2O$$

SODIUM AMIDE

Sodium amide is another chemical that has found many special uses in organic chemistry. It is a vigorous dehydrating agent and, for this reason, is used in the synthesis of indigo and in the preparation of pure hydrazine. It is also an intermediate in the preparation of sodium cyanide and finds application as an aminating agent.

It is prepared by passing ammonia into metallic sodium at 200 to 300°C.

$$NH_3 + Na \rightarrow NaNH_2 + \tfrac{1}{2}H_2$$

This reaction may be carried out in iron equipment; in many cases a ball-mill type reactor[2] is satisfactory. This compound should be handled with care as it decomposes with water explosively. Also it should not be kept, as disastrous explosions have resulted from handling material that had been stored. It should be consumed as made.

SODIUM CYANIDE

Sodium cyanide is not only important in the inorganic and organic chemical fields but also has many metallurgical applications. It is used in treating gold ore, the casehardening of steel, in electroplating, in organic reactions, and for the preparation of hydrocyanic acid. Sodium cyanide can be made from sodium amide heated with carbon at 800°C., the carbon as charcoal being thrown into the molten sodium amide.

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[1] See Boron Compounds in Chap. XXI.

[2] Shreve, Riechers, Rubenkoenig, and Goodman, Aminations by Sodium Amide, *Ind. Eng. Chem.*, **32**, 173 (1940).

$$NaNH_2 + C = NaCN + H_2$$

Another method of manufacture is to melt together sodium chloride and calcium cyanamide in an electric furnace. The most recent commercial method consists of the dehydration of formamide by heat and a catalyst into hydrocyanic acid. The hydrocyanic acid is then converted to sodium cyanide by treatment with caustic soda.

$$HCONH_2 \rightarrow HCN + H_2O$$
$$HCN + NaOH \rightarrow NaCN + H_2O$$

Problems

1. 1,000 lb. of rasorite containing 85 per cent $Na_2B_4O_7 \cdot 4H_2O$ is redissolved, filtered, and run to the crystallizer as a 20 per cent solution of borax, $Na_2B_4O_7 \cdot 10H_2O$, at 175°F. After cooling to 110°F. the crystals are centrifuged and go to the drier carrying 6 per cent moisture. The mother liquor contains 10 per cent borax. What yield of dry crystals is obtained?

2. In the evaporation of salt brines a certain manufacturer uses a triple-effect evaporator with parallel feed. Fifty per cent of the feed sent into each effect is evaporated. Eight thousand pounds of saturated steam per hour at 230°F. is sent into the first effect. Brine is sent into first effect at 70°F.

	Effect		
	I	II	III
Boiling point, °F.	210	180	125
Area, sq. ft.	500	500	500

Calculate

a. Capacity of the evaporator.
b. Steam economy.
c. Over-all coefficient for each effect.

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Snell, F. D., and C. T. Snell, "Chemicals of Commerce," D. Van Nostrand Company, Inc., New York, 1939.

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Ullmann, Fritz, "Enzyklopaedie der technischen Chemie," 10 vols., 2d ed., Urban & Schwarzenberg, Berlin and Vienna, 1928–1932.

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CHAPTER XV

SODA ASH, CAUSTIC SODA, AND CHLORINE

The manufacture of soda ash, caustic soda, and chlorine is one of the most important heavy chemical industries. These chemicals rank next to sulfuric acid in quantity produced and in wide diversity of use. Soda ash finds application in glass, soaps, pulp and paper, textiles, and water softeners as well as in the manufacture of caustic soda, sodium phosphates, and sodium bicarbonate. Caustic soda from soda ash and from the electrolysis of salt brine is consumed in large quantities in the manufacture of rayon, explosives, soap, paper, and in many other processes. The demand for chlorine has developed phenomenally in the past decade.

Historical.—The present process for the manufacture of soda ash is the Solvay process. Before this method was developed, the LeBlanc process was in universal use. Nicholas LeBlanc devised his famous process for soda ash manufacture around 1773.[1] It was based on roasting salt cake with carbon and limestone in a rotary furnace, with subsequent leaching of the product with water. The reactions were

$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$$
$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2$$
$$Na_2S + CaCO_3 \rightarrow Na_2CO_3 + CaS$$

The crude product of the reaction was called *black ash.* It was leached cold, whereupon some hydrolysis of sulfides took place. These were changed to carbonate by treatment with the carbon dioxide containing gases from the black ash furnace. The resulting sodium carbonate solution was concentrated to obtain crystalline sodium carbonate,[2] which was then dried or calcined. No LeBlanc plant was ever built in the United States, and none is now being operated anywhere in the world.

In 1869 Ernest Solvay began developing the ammonia-soda process. At first this method had great difficulty in competing with the older and more established LeBlanc process. But in a few years the Solvay process reduced the price of soda ash to almost one-third the original price. After a struggle during which the producers of LeBlanc soda sold at a loss for many years, the ammonia-soda process completely had displaced the LeBlanc by 1915.

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[1] Hou, "Manufacture of Soda," 2d ed., Reinhold Publishing Corporation, New York, 1942. For further details on alkali and chlorine production, see also Chap. 10 by the same authority in "Rogers' Manual of Industrial Chemistry," D. Van Nostrand Company, Inc., New York, 1942.

[2] A flow sheet of this obsolete process is given in Badger and Baker, "Inorganic Chemical Technology," 2d ed., p. 137, McGraw-Hill Book Company, Inc., New York, 1941.

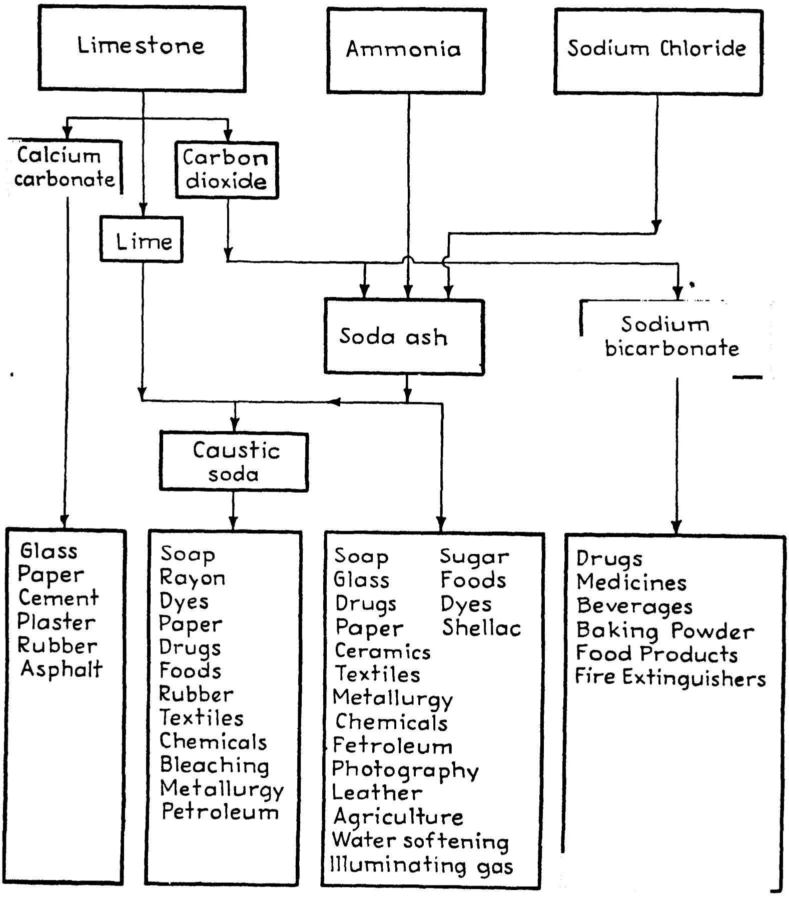

FIG. 1.—Alkali industry chart.

The electrolytic production of caustic soda was known in the eighteenth century, but it was not until 1890 that caustic was actually produced in this way for industrial consumption. Electrolytic chlorine developed with electrolytic caustic and at present is the more valuable of the two products. The use of commercially fixed chlorine, in the form of bleaching powder, had been developed earlier with chlorine made from the oxidation of HCl with air, catalyzed by MnO_2 or by Cu_2Cl_2.[1]

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[1] Reaction: $4HCl + O_2 \rightarrow 2H_2O + 2Cl_2$. U.S. Pat., 85370 (1868); *cf.* BADGER and BAKER, *op. cit.* p. 186.

The first American production of electrolytic chlorine was at Rumford Falls, Me., in 1893.[1] Electrolytic caustic and chlorine require cheap electricity and a ready source of salt. For this reason a large number of plants are located near Niagara Falls and in West Virginia.

TABLE 1.—U.S. PRODUCTION OF SODA ASH IN SHORT TONS[a]

1931	2,275,416
1935	2,508,859
1937	3,037,421
1940	3,157,000
1941	3,746,000
1942	3,934,000
1943	4,543,000

[a] *Chem. & Met. Eng.*, **48**, No. 2, 94 (1941); *Chem. & Met. Eng.*, **51**, No. 2, 113 (1944).

Uses and Economics.—*Soda ash* is a lightweight solid, readily soluble in water, and usually contains 99.2 per cent Na_2CO_3. It is sold on the basis of the sodium oxide content which is generally 58 per cent. It is used in the manufacture of many chemicals, the most important of which are caustic soda and sodium bicarbonate. It also crystallizes with water to form $Na_2CO_3 \cdot 10H_2O$ which is known as *sal soda* or *washing soda*. Besides the applications listed in Table 2 and Fig. 1, another recent use for soda ash is as a desulfurizing agent in ferrous metallurgy. The 1943 selling price was $21 per ton. Of the 4,562,000 tons of soda

TABLE 2.—ESTIMATED DISTRIBUTION OF SODA ASH IN UNITED STATES IN 1941, 1942, AND 1943[a]

(In thousands of short tons)

	1941	1942	1943
Glass	990	1,100	1,200
Soap	170	165	150
Caustic and bicarbonate	1,033	960	1,010
Other chemicals	800	840	950
Cleansers and modified sodas	70	80	85
Pulp and paper	155	145	155
Water softeners	70	80	95
Petroleum refining	23	18	20
Textiles	60	56	58
Exports	85		
Miscellaneous	140	230	370
Nonferrous metals	150	260	450
Totals	3,746	3,934	4,543

[a] *Chem. & Met. Eng.*, **51**, No. 2, 113 (1944).

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[1] BALDWIN, The History of Chlorine Industry, *J. Chem. Education*, **4**, 313–319 (1927).

ash produced in 1943, 4,380,000 tons were ammonia soda, 164,000 tons natural soda, and 18,000 tons electrolytic soda.

Pure *caustic soda* is a brittle white solid which readily absorbs moisture and carbon dioxide from the air. It is sold on the basis of its sodium oxide content and usually contains about 76 per cent Na_2O or 98 per cent NaOH. Special uses, such as in rayon manufacture, require very pure caustic. It is shipped either as a solid or as a 50 per cent solution in tank cars. At present there is a tendency toward shipping more caustic as concentrated solutions. The price of solid caustic soda in 1942 was $55 per ton.

TABLE 3.—UNITED STATES PRODUCTION OF CAUSTIC SODA[a]
(In short tons of 100 per cent NaOH)

	Lime soda	Electrolytic	Total
1921	163,044	75,547	238,591
1923	314,195	122,424	436,619
1925	355,783	141,478	497,261
1927	387,235	186,182	573,417
1929	524,985	236,807	761,792
1931	455,832	203,057	658,887
1933	439,363	247,620	686,983
1935	436,980	322,401	759,381
1937	488,807	479,919	968,726
1939	532,914	512,492	1,045,406
1940 (est.)	505,000	595,000	1,100,000
1941	685,999	743,316	1,429,310
1942	634,291	939,878	1,514,169
1943	673,495	1,036,564	1,710,059
1944 (4 mo.)	266,367	395,106	661,473

[a] Figures for 1921–1943, except 1940, are from the U.S. Bureau of the Census. Electrolytic caustic soda figures up to 1941 do not include that made and consumed at wood-pulp mills, estimated at about 30,000 tons in 1927 and 1929, 24,000 tons in 1931, 21,000 tons in 1933, 20,000 tons in 1934, 17,000 tons in 1935, 19,000 tons in 1936 and 1937, 18,000 tons in 1938, 25,000 tons in 1939, and 30,000 tons in 1940. Figures for 1941–1944 include production at pulp mills. Do not include production at government-owned plants, all of which are electrolytic.

Chlorine is a chemical of wide importance industrially. It is used for the manufacture of bleaching powder, in bleaching operations, in the sterilization of water supplies, the treatment of sewage, the chlorination of ores, and in the manufacture of many organic chemicals. Considerable chlorine is consumed at the plants where it is produced, but much more is dried and shipped in steel tanks as liquid chlorine. Of the 1,200,000 tons of chlorine obtained in 1943 approximately 1,070,000 tons were produced with electrolytic caustic and 130,000 tons from the manufacture of caustic potash, metallic sodium, Solvay's nitrosyl chloride process, and other sources.[1]

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[1] *Chem. & Met. Eng.*, **51**, No. 2, 119 (1944).

TABLE 4.—ESTIMATED DISTRIBUTION OF CAUSTIC SODA IN THE UNITED STATES, 1935–1943[a]
(In short tons)

Consuming industries	1935	1936	1937	1938	1939	1940	1941	1942	1943
Soap	96,000	104,000	94,000	95,000	100,000	103,000	125,000	120,000	105,000
Chemicals	118,000	130,000	173,000	138,000	187,000	212 000	260,000	300,000	360,000
Petroleum refining	81,000	88,000	82,000	80,000	99,000	105 000	116,000	100,000	130,000
Rayon, staple fiber, and cellulose film	163,000	170,000	186,000	156,000	196,000	230,000	270,000	300,000	320,000
Lye and cleansers	38 000	46,000	48,000	40 000	44,000	48 000	52,000	70,000	100,000
Textiles	34 000	43,000	45 000	36,000	44,000	48 000	63,000	110,000	120,000
Rubber reclaiming	11,000	14,000	17,000	11,000	18,000	15 000	18,000	20 000	24,000
Vegetable oils	14,000	14,500	20 000	21,000	17 000	16 000	20,000	19,000	19,000
Pulp and paper	38,000	43 000	48,000	37 000	47 000	78 000	100 000	85,000	95,000
Exports	69,500	77,000	102,000	101,000	130,000	105 000	120 000	[b]	[b]
Miscellaneous	56 500	63,500	173 000	150,000	143,000	158 000	230,000	340 000	510,000
Total	719 000	793,000	988,000	865,000	1,025,000	1,118 000	1,374,000	1,464,000	1,783,000

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[a] *Chem & Met Eng*, **51**, No 8 115 (1944)

[b] In 1942 and 1943, exports are included under Miscellaneous.

TABLE 5.—PRODUCTION AND CONSUMPTION OF CHLORINE BY PRIVATELY OWNED PLANTS[a]
(In short tons)

	Production	Consumption at producing plants
1937	446,261	160,301
1939	514,401	175.126
1941	797,976	396,079
1942	987,784	557,796
1943	1,211,720	698,767
1944 (5 mo.)[b]	532,323	314,888

[a] *Chem. & Met. Eng.*, **48**, 97 (1941); *Chem. & Met. Eng.*, **51**, No. 2, 119 and No. 8, 115 (1944). These figures include the chlorine made and used in paper mills, but do not include that in government plants. Data from U.S. Bureau of Census.

[b] Preliminary.

MANUFACTURE OF SODA ASH

Soda ash is manufactured chiefly by the Solvay or ammonia-soda process. Some natural soda ash is obtained from the brines of saline lakes in the West.

Raw Materials.—The raw materials for the Solvay process are salt, lime, and ammonia. The salt is used in the form of a brine which is made from rock salt, natural or artificial brine, or from sea salt. Limestone is burned in kilns to furnish both the carbon dioxide for the soda ash and lime for the recovery of the ammonia. No strict specifications are required for the limestone except that a minimum of the usual impurities of SiO_2, Al_2O_3, and Fe_2O_3 is desirable.

Reactions and Energy Changes.—The Solvay process is carried out by the following principal reactions:

$$CaCO_3 \rightarrow CaO + CO_2; \quad \Delta H = +43{,}500 \text{ cal.} \tag{1}$$

$$C \text{ (amorph.)} + O_2 \rightarrow CO_2; \quad \Delta H = -96{,}500 \text{ cal.} \tag{2}$$

$$CaO + H_2O(l) \rightarrow Ca(OH)_2(s); \quad \Delta H = -15{,}900 \text{ cal.} \tag{3}$$

$$NH_3(g) + H_2O(l) \rightarrow NH_4OH(aq); \quad \Delta H = -8{,}400 \text{ cal.} \tag{4}$$

$$2NH_4OH(aq) + CO_2 \rightarrow (NH_4)_2CO_3(aq) + H_2O(l); \quad \Delta H = -22{,}100 \text{ cal.} \tag{5}$$

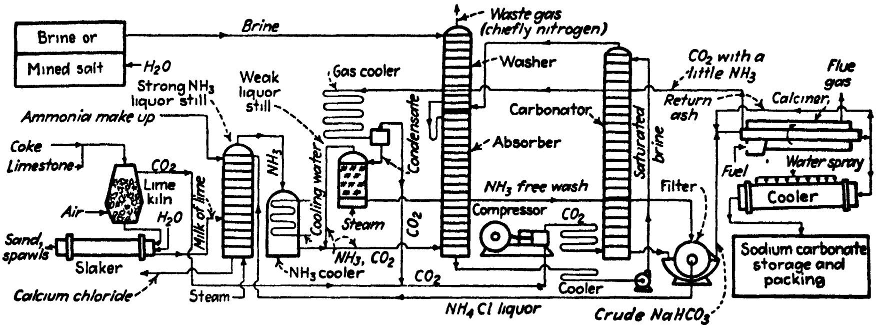
$$(NH_4)_2CO_3 + CO_2 + H_2O \rightarrow 2NH_4HCO_3 \tag{6}$$

$$NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3 \tag{7}$$

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g); \quad \Delta H = +30{,}700 \text{ cal.} \tag{8}$$

$$2NH_4Cl(aq) + Ca(OH)_2(s) \rightarrow 2NH_3(g) + CaCl_2(aq) + 2H_2O(l); \quad \Delta H = +31{,}800 \text{ cal.} \tag{9}$$

Unit Operations and Unit Processes.—The reactions are industrialized by the following sequence of *unit operations* (Op.) and *unit processes* (Pr.) as exemplified in the flow sheet[1] of Fig. 2.



Salt	150-175 tons	Per ton of 58% soda ash Capital Investment $12,000 per daily ton capacity
Limestone	120-135 tons	
Coke	0095-011 tons	
Coal (boilers)	025- 05 tons	
Coal (dryers)	016- 025 tons	
NH_3 loss	2-4 kg as $(NH_4)_2SO_4$	
CO_2	1,000-1,200 cu ft	
Na_2S	0001 0002 ton	
Cooling water	15,000-18,000 gal	
Direct labor	2 man-hr	
Repair and maintenance	26 man-hr	

FIG. 2.—Flow sheet for the manufacture of soda ash by the ammonia-soda process.

Preparation of the Salt Brine:

Mining and solution of salt, or pumping of water to salt beds and of brine from these deposits (Op.).

Purification of brine (Pr. and Op.).

Ammoniation of Brine:

Solution of NH_3 in the purified brine (Op. and Pr.).

Solution of weak CO_2 in the purified brine (Op. and Pr.).

Carbonation of Ammoniated Brine:

Formation of ammonium carbonate (Pr.).

Formation of ammonium bicarbonate (Pr.).

Formation and controlled precipitation of sodium bicarbonate (Pr.).

Filtration and washing of the sodium bicarbonate (Op.).

Burning of limestone with coke to form CO_2 and CaO (Pr.).

Compressing and cooling of limekiln or lean CO_2 and piping to carbonator (Op.).

Calcination of Sodium Bicarbonate:

Conveying and charging of moist sodium bicarbonate to calciner (Op.).

Calcination of sodium bicarbonate (Pr. and Op.).

Cooling, screening, and bagging of soda ash (for sale) (Op.).

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[1] See also the pictured flow sheet, *Chem. & Met. Eng.*, **49**, No. 2, 134 (1942).

Cooling, purifying, compressing, and piping of rich CO_2 gas to carbonator (Op.).

Recovery of Ammonia:

Slaking of quicklime (Pr.).

Treatment of sodium bicarbonate mother liquors with steam and $Ca(OH)_2$ in strong NH_3 liquor still to recover NH_3 (Pr.).

Manufacturing Procedures. *Preparation of the Brine.*—The salt used in the process is in the form of an almost saturated NaCl solution as a natural or artificial brine pumped from wells. Such brines come usually from underground salt deposits. Sea water contains much more impurity than does the rock salt brine and is seldom employed. The chief impurities in rock salt brine are calcium sulfate, magnesium, and iron salts. These may be removed by special pretreatments of the brine with lime and soda ash as well as by the ordinary precipitation with weak ammonia and weak carbon dioxide in the washer tower where residual gases are scrubbed or washed before discharge. Although Fig. 2 does not so indicate, the brine is clarified by settling in vats before it flows to the strong ammonia absorber, to remove the precipitated impurities of calcium carbonate, magnesium carbonate and hydroxide, and iron hydroxide. The clarified brine is also cooled.

Ammoniation of Brine.—The clarified brine flows to the strong ammonia or first absorber where it takes up the necessary amount of ammonia. The ammoniation liberates much heat from the dissolving of the NH_3 gas as shown by reaction (4). This brine contains about 83 grams of NH_3 and 260 grams of NaCl per liter. Some carbon dioxide is also absorbed with the ammonia. The brine is settled, cooled to 25°C., and pumped to the carbonating towers.

Carbonation of Ammoniated Brine.—Carbon dioxide is obtained along with calcium oxide by calcining limestone *mixed* with coke. Thus some additional carbon dioxide is yielded from the burning of the coke necessary to supply the heat required to decompose the limestone. At least a part of this carbon dioxide gas, 41 to 43 per cent strong, is compressed and conducted to the bottom of a fouled carbonating tower, operating in series with three working or precipitating towers, while the ammoniated brine is fed into the top. In this way, the towers, clogged and fouled by 4 days' service as "making" or precipitating towers, are cleaned by solution in fresh ammoniated brine of the crusts of sodium bicarbonate previously deposited on the baffles and cooling pipes. *Thus the heat transfer rate is increased by removal of the fouling on the interfaces; likewise the absorption of the carbon dioxide is improved by solution of the crusts that interfered with the contact of gas and liquid.* In practice, the fresh ammoniated brine flows down one such fouled tower with its cooling coils shut off, and this partly carbonated and warm brine is fed to four making towers by carbon dioxide lifts. In the first carbonating tower reaction (5) takes place forming ammonium carbonate in solution. Each carbonating tower is about 75 ft. high, 6 or 7 ft. inside diameter, and is constructed largely of cast-iron sections bolted together. Typical absorbing and cooling sections of such a tower are illustrated in Fig. 3. The absorption is not very efficient. Hence a comparatively great height is needed. In the second or making tower[1] ammonium bicarbonate is formed and, reacting with salt, forms sodium bicarbonate which is gradually precipitated out.[2] The rich carbon dioxide (90 to 95 per cent) from the calcination of the sodium bicarbonate is compressed and used here. Each making tower produces the equivalent of about 50 tons of soda ash per 24 hr.

The procedure in these towers is the heart of the ammonia-soda process. It is a liquid-gas absorption but is complicated by the precipitation of the solid sodium bicarbonate. The absorption units should be constructed to permit the downward travel of the growing sodium bicarbonate crystals. This is done as shown in Fig. 3 by having each unit simulate a very large *single* bubble cap with down sloping floors.

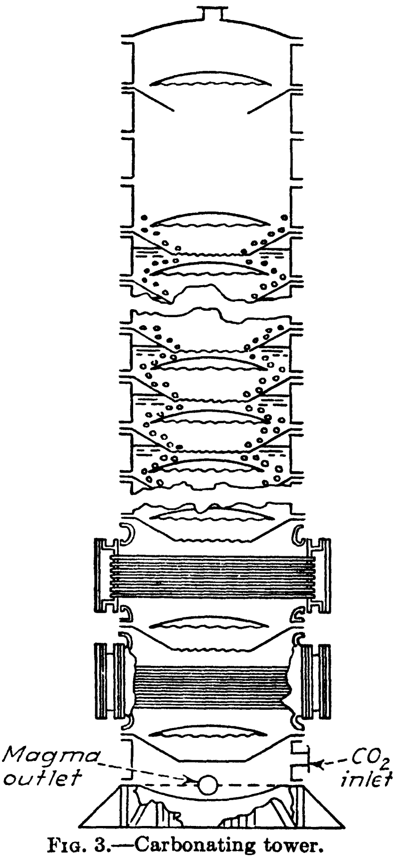

Fig. 3.—Carbonating tower.

Also, the absorption is conducted with the towers *filled* with liquid, hence the gas must be compressed. Because of this compression the partial pressure, hence the solubility, of the CO_2 is increased at the end of the carbonating cycle where it favors reactions (5) to (7).

The crude sodium bicarbonate formed in the making tower is drawn off from the bottom as a suspension. Careful control of all the conditions in the column is necessary to ensure that the precipitated sodium bicarbonate is easily filterable and efficiently washed. This is largely effected by regulating the temperature and concentration in the making tower so that the initially formed fine crystals of $NaHCO_3$ are allowed to grow. For example, at the top of the making tower the temperature is 25°C., which is allowed to rise by heat of reaction to 55°C. about halfway down. This temperature is gradually reduced by use of cooling sections (see Fig. 3) to 20°C. at bottom, resulting in the growing of the $NaHCO_3$ crystals particularly in size. The suspension is filtered on a rotary open-drum filter. The vacuum on the drum filter helps to dry the bicarbonate and also to recover the ammonia. The filter cake is washed on the drum to remove salt and ammonium chloride. About 10 per cent of the bicarbonate is dissolved during the washing. From here the sodium bicarbonate may be sent to a centrifugal filter which reduces the moisture content to about 7 per cent, or it may be calcined directly.

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[1] Figure 2 for simplicity makes no separation of the lean from the rich CO_2 gas—as is the actual practice in a few plants—nor does this figure differentiate between the cleaning and "making" carbonations.

[2] Sherwood, "Absorption and Extraction," pp. 217–220, McGraw-Hill Book Company, Inc., New York, 1937.

Calcination or "Drying" of the Sodium Bicarbonate.—This operation is one of the most troublesome steps in the manufacture of soda ash. The washed, moist sodium bicarbonate from the filter is charged into the furnace by feed tables which have an efficient gas seal. The difficulties are due to the fact that moist sodium bicarbonate has a tendency to cake into lumps and form a nonconducting scale on the steel shell of the calciner. Engineers have developed for this operation a steel rotary furnace closed at both ends so as to be able to collect the gases evolved. The kiln is of the horizontal type heated through the shell and with the firing furnace at the feed end so that the heating is not countercurrent. This prevents some of the caking. The inside of the drier has a heavy scraper chain dragging on the shell to keep it free from soda lumps. To reduce the caking of the wet bicarbonate some of the hot soda ash taken from the calciner is fed back and mixed with the fresh bicarbonate as "dry feed" (see Fig. 2). The usual capacity for the rotary driers, about 8 ft. in diameter and 75 ft. long, is from 50 to 60 tons of soda ash per 24 hr.

The exit gases contain some ammonia, carbon dioxide, much steam, and a little soda ash dust. These are cooled, precipitating a small quantity of an aqueous ammoniacal solution but permitting the large amount of rich CO_2 to be freed. This is compressed and used in the making carbonator tower to form the sodium bicarbonate. The hot soda ash from the calciner is passed through a rotary cooler and is screened through a vibrating screen of 8 to 12 mesh. It is then packed in bags for sale. This is the light ash of commerce. The coarser or dense soda ash occupies only about half the bulk of the light ash, the dense ash weighing 64 to 67 lb. per cu. ft. when loosely packed. It costs slightly more but this dense ash is advantageous for the glass industry where less dusting results. The dense ash is manufactured by adding sufficient water to the light soda ash to form $Na_2CO_3{\cdot}H_2O$, an agglomerated product, whose recalcination furnishes the dense ash.

Recovery of the Ammonia.—Much of the economical operation of the Solvay process depends upon the efficiency of the ammonia recovery. For any given time the value of the ammonia in the system is several times the value of the soda ash produced. The ammonia is recovered in a distillation column called the *strong ammonia liquor still* and consisting of two parts. The top part above the lime inlet is called the *heater;* the bottom part below the lime inlet is called the *lime still.* The liquor from the bicarbonate filter is fed into the heater or upper part of the ammonia still, where the free ammonia is driven out by the following reactions:

$$\begin{gathered}
NH_3(\text{soln.}) + \text{heat} \rightarrow NH_3(g) \\
NH_4HCO_3 + \text{heat} \rightarrow NH_3 + H_2O + CO_2 \\
NaHCO_3 + NH_4Cl \rightarrow NaCl + NH_3 + H_2O + CO_2 \\
Na_2CO_3 + 2NH_4Cl \rightarrow 2NaCl + 2NH_3 + H_2O + CO_2 \\
Na_2S + 2NH_4Cl \rightarrow 2NaCl + 2NH_3 + H_2S
\end{gathered}$$

Milk of lime suspension is fed through the lime inlet and mixes with the liquor from the upper or heater part. As this flows down the column, the following reactions take place in the lime part of the still:

$$\begin{gathered}
Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3 \\
2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + H_2O \\
(NH_4)_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2NH_3 + 2H_2O
\end{gathered}$$

The liquor from the bottom of the lime still is free from ammonia and contains about 50 grams per liter of residual and unreacted sodium chloride as well as the calcium chloride formed. Calcium carbonate is in suspension. A small part of this residual liquor is settled, evaporated for separation of salt, and marketed for its calcium chloride content either as a concentrated liquor or as a solid upon further evaporation. However, most of this calcium chloride is wasted into the streams of the country.

Soda ash is manufactured from natural alkaline *brines* at Searles Lake and Owens Lake in California.[1] The natural brine is carbonated with carbon dioxide from limekilns and from sodium bicarbonate calciners. The precipitated $NaHCO_3$ is filtered off, washed, and calcined.

MANUFACTURE OF SODIUM BICARBONATE

Sodium bicarbonate, or baking soda, is not made by refining the crude sodium bicarbonate obtained from the filters in the Solvay process.

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[1] MANNING, Chemicals from California's Desert, *Chem. & Met. Eng.*, **48,** 96 (1941).

There are several reasons for this: (1) There is great difficulty in completely drying this bicarbonate. (2) The value of the ammonia in this crude bicarbonate would be lost. (3) Even a small amount of ammonia gives the bicarbonate an odor that renders it unfit for many uses. (4) The bicarbonate made in this way contains a great many other impurities.

To make sodium bicarbonate, there is first prepared a saturated solution of soda ash which is run into the top of a column similar to the carbonating tower in soda ash manufacture. Carbon dioxide is sent in from compressors at the bottom of the tower, which is maintained at about 40°C. The suspension of bicarbonate formed is removed from the bottom of the tower, filtered, and washed on a rotary drum filter. After centrifugation, the material is dried on a continuous belt conveyer at 70°C. Bicarbonate from this process is about 99.9 per cent pure.

Sodium bicarbonate finds large usage for the manufacture of baking powder, carbonated waters, leather goods, and in fire extinguishers. Annually around 100,000 tons are manufactured in the United States with a valuation of about $30 per ton.

MISCELLANEOUS ALKALIES

There are consumed commercially a number of various alkalies of different strengths according to the contained amounts of NaOH, Na_2CO_3, or $NaHCO_3$. Some of these are mechanical mixtures as *causticized ash* (soda ash with 10 to 50 per cent of caustic) for bottle washing or metal cleaning, and *modified sodas* (soda ash with 25 to 75 per cent of sodium bicarbonate) for mild alkali demands as in the tanning industry. *Sodium sesquicarbonate,* or the natural mineral trona, has the composition $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ and is very stable. It finds use in wool scouring and in laundering. *Sal soda,* $Na_2CO_3 \cdot 10H_2O$, is also known as *washing soda* or *soda crystals.* It has always been a pure product, but its consumption is declining because of the cost of transporting its water of crystallization in competition with the now quite pure soda ash manufactured by the ammonia-soda process.

MANUFACTURE OF CAUSTIC SODA BY THE LIME-SODA PROCESS

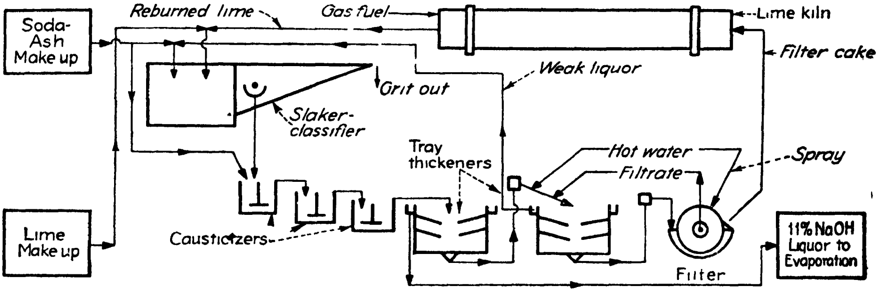
Caustic soda is one of the main products from soda ash and is frequently made in the soda ash plant. The production of additional carbon dioxide frequently needed for the Solvay process furnishes calcium oxide used in the causticization of the soda ash.

$$Na_2CO_3 + Ca(OH)_2 \rightleftarrows 2NaOH + CaCO_3; \qquad \Delta H = -2{,}100 \text{ cal.}$$

This reaction depends on the low solubility product of Ca^{++} and CO_3^{--} ions, forming calcium carbonate. The equilibrium varies with the concentration of the Na_2CO_3 solution, a 10 per cent soda solution giving a 97 per cent conversion while a 16 per cent Na_2CO_3 solution furnishes only a 91 per cent conversion.[1] The equation for this is as follows:

$$K = \frac{K_1}{K_2} = \frac{(Ca^{++})(OH^-)^2}{(Ca^{++})(CO_3^{--})} \quad \frac{(OH^-)^2}{(CO_3^{--})}$$

As the heat change of this reaction is so low, the K and hence the equilibrium are but little affected by temperature. However both the *speed* of the reaction and the rate of settling of the $CaCO_3$ increase with the temperature. Hence, in practice, the reaction is carried out near the boiling point of the solution. The higher percentage of conversion at the more dilute solution also follows from this equation since the concentration of the hydroxyl ions varies as the square in relation to the first power of the concentration of the carbonate ions. The chemical engineer in charge of causticizing soda ash must balance the additional fuel and plant charges for concentrating the more dilute caustic against the advantages of the greater conversion of the more dilute carbonate solution. At soda ash plants, usually the crude bicarbonate directly from the rotary filters is dissolved in water and changed to the carbonate by boiling with steam. The carbon dioxide evolved is returned to the soda ash process.



Soda Ash (58%)	2900 lb
Lime make-up (90% CaO)	160 lb
Water	18000 lb
Steam	2,700 lb
Reburning fuel	13,000,000 B.t.u.
Electricity	18 kw-hr
Direct labor	0.9 man-hr

Per ton NaOH in 11% solution (plant capacity 100 tons/day)

FIG. 4.—Flow sheet for caustic soda solution by Dorr continuous lime-soda process.

The Dorr continuous, countercurrent decantation procedure is illustrated in Fig. 4, where a solution of sodium carbonate is made in an agitated tank using weak liquor from a former reaction. Reburned lime and make-up lime, or all fresh lime, is fed along with some of the soda ash solution to a combination classifier-slaker. Milk of lime is formed while grit is removed from the slurry by the classifier.

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[1] Hou, *op. cit.*, Chap. 19. The mathematical treatment of this equilibrium is here presented.

The soda solution is causticized with a slight excess of lime in three agitators in series. The solution is settled in thickeners,[1] usually of multitray design as shown in Fig. 4. The overflow solution taken from the first thickener is sent to the evaporators or is used directly as in the soda process for paper pulp manufacture. This solution contains about 11 per cent NaOH. The sludge in the bottom of the first thickener is pumped with a diaphragm pump to the second thickener. Here filtrate from the next operation and water are added. The overflow from this thickener is used as a weak liquor to make up the original soda solution. The sludge from the second thickener is filtered on an Oliver filter and washed. The filtrate is returned to the second thickener as mentioned and the cake is calcined in the limekiln.[2]

The evaporation of caustic from soda ash causticization resembles that from electrolysis of brine (see Fig. 5, and text) except that here only one-twentieth to one-tenth of the sodium salts is present to crystallize out upon concentration of the NaOH solution. In this case the sodium salts recovered consist mostly of unreacted Na_2CO_3 with whatever NaCl was in the original soda ash.

A recent development in the removal of water is the use of kerosene in a partial pressure process.[3] Kerosene or some other hydrocarbon is fed into a caustic evaporator and is distilled out, taking the water with it. This serves to remove the water at a temperature much lower than the usual caustic fusion process. This method claims lower heat requirements, continuous operation, and the production of a crystalline product.

MANUFACTURE OF ELECTROLYTIC CAUSTIC SODA AND CHLORINE

Raw Materials.—The primary raw material for the manufacture of chlorine and electrolytic caustic is common salt which is available in large quantities and high purity in many parts of the United States. Some plants, like those in the Kanawha Valley of West Virginia or in the salt belt of Michigan, obtain their salt from the natural brines of underground deposits, while other plants, such as around St. Louis, ship in salt from mines located elsewhere and make the brine at the plant.

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[1] For details of Dorr thickener and Dorr multitray thickener, see Perry, *op. cit.*, pp. 1626, 1628.

[2] Frequently another Dorr thickener is required to remove more of the caustic from the precipitated $CaCO_3$. Calculations of countercurrent decantation (c.c.d.) as applied to this reaction are exemplified on pp. 154*ff.* of Badger and Baker *op. cit.* See also Olsen and Direnga, Settling Rate of Calcium Carbonate in Causticizing of Soda Ash, *Ind. Eng. Chem.*, **33**, 204 (1941). The methods, equipment, and examples given in Perry, *op. cit.*, pp. 1626–1630, 1643–1650, 1673, 1691 are particularly pertinent.

[3] OTHMER and JACOBS, Anhydrous Sodium Hydroxide, *Ind. Eng. Chem.*, **32**, 154 (1940).

In California, salt is obtained from the evaporation of sea water. Other raw materials are listed on the lower part of the flow sheet in Fig. 5.

Reactions and Energy Changes. *Decomposition Voltage and Voltage Efficiency.*—The energy consumed in the electrolysis of the brine is the product of the current flowing and the potential of the cell. The *theoretical* or minimum *voltage* required for the process may be derived from the Gibbs-Helmholtz equation which expresses the relation between the electrical energy and the heat of reaction of a system:

$$E = \frac{J\Delta H}{F} - \frac{TdE}{dT}$$

where E = theoretical decomposition voltage.

ΔH = enthalpy change of reaction, cal. per gram-equivalent ($\Delta H = -Q$ where Q = heat of reaction).

J = electrical equivalent of heat, or joules per calorie (4.182).

T = absolute temperature.

F = Faraday constant, coulombs per gram-equivalent (96,500).

The heat of reaction for the electrolysis of salt may be found from heats of formation of the components of the over-all reaction or from the negative of these values—the change in the heat contents of the systems. The over-all reaction is

$$NaCl(aq) + H_2O(l) \rightarrow NaOH(aq) + \tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g)$$

this may be broken down to the following reactions of formation:

$$Na(s) + \tfrac{1}{2}Cl_2(g) \rightarrow NaCl(aq); \qquad \Delta H = -97{,}105 \text{ cal.}$$
$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l); \qquad \Delta H = -68{,}372 \text{ cal.}$$
$$Na(s) + \tfrac{1}{2}O_2(g) + \tfrac{1}{2}H_2(g) \rightarrow NaOH(aq); \qquad \Delta H = -112{,}053 \text{ cal.}$$

The net ΔH for the over-all reaction results from

$$+97{,}105 + 68{,}372 - 112{,}053 = +53{,}424 \text{ cal.}$$

If this value of ΔH is substituted in the Gibbs-Helmholtz equation and the change in voltage with temperature is neglected, the value of E calculates to 2.31 volts. The omission of $T \cdot dE/dT$ involves an error of less than 10 per cent for most cells.[1]

The ratio of this theoretical voltage to that actually used is the *voltage efficiency* of the cell. Voltage efficiencies range from 45 to 65 per cent. According to Faraday's law 96,500 coulombs of electricity passing through a cell will produce 1 gram-equivalent of chemical reaction at each elec-

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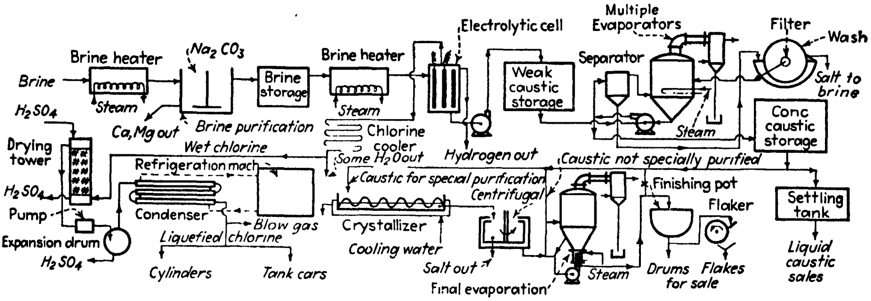
[1] BADGER and BAKER, *op. cit.*, p. 165. *Cf.* PERRY, *op. cit.*, pp. 2746, 738, 636 and Tables pp. 547–565.

trode. Because of unavoidable side reactions, cells usually require more than this amount. The ratio of the theoretical to the actual current consumed is defined as the *current efficiency*. Current efficiencies run 95 to 97 per cent and, unless otherwise specified, are understood to be *cathode* current efficiencies. The current divided by the area in square inches, upon which the current in amperes acts, is known as the *current density*. A high value is desirable in cases where the product formed is subject to decomposition. The product of voltage efficiency and current efficiency gives the *energy efficiency* of the cell. Another consideration is the *decomposition efficiency*, which is the ratio of equivalents produced in the cell to equivalents charged.[1] In the usual commercial cells this decomposition efficiency is about 50 per cent. If the cell is operated to attain a higher decomposition efficiency, the natural flow of brine through the cell is decreased with migration of OH^- ions back to anode with formation of hypochlorite which means loss of caustic and chlorine. Also when OH^- ions reach the anode the following reaction occurs:



Salt	16 tons	Electricity	2,500 Kw.-hr.	Per ton 76% caustic plus 1,750 lb. chlorine and 8,750 cu.ft hydrogen
Sodium carbonate (58%)	50 lb	Refrigeration	09 ton	
Sulfuric acid (66°Be')	200 lb.	Direct labor	18 Man-hr	
Steam	20,000 lb.	Production, daily	75 tons caustic	(50 lb. H_2)

FIG. 5.—Flow sheet for electrolytic caustic soda and chlorine.

$$2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e$$

The oxygen formed reacts with the graphite of the anodes causing decreased anode life.

Unit Operations and Unit Processes.—The main procedures for a typical electrolytic flow sheet,[2] as depicted in Fig. 5, may be represented in the following *unit operations* (Op.) and *unit processes* (Pr.):

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[1] A tabulation of such data for typical commercial cells is given by Perry, *op. cit.*, p. 2796.

[2] Further details as to the varied procedures used may be found on pp. 159*ff.* of Badger and Baker, *op. cit.* In this book there is a particularly fine and detailed presentation of the evaporation of caustic soda and of the equipment required. See also the pictured flow sheet, *Chem. & Met. Eng.*, **49**, No. 12, 118 (1942).

Brine Purification:

To make a purer caustic soda and to lessen clogging of the cell diaphragm with consequent voltage increase, purification of the NaCl solution from Ca and Mg compounds is practiced, using soda ash with some caustic soda. Sometimes sulfates are removed with $BaCl_2$. The clear brine is neutralized with hydrochloric acid (Pr.). This brine is stored, heated, and fed to the cells through a float feed system, designed to maintain constant level in the anode compartments (Op.).

Brine Electrolysis:

Typical cells employed are depicted and described in the following section. Each cell usually requires 3.5 to 4.5 volts; consequently, 30 or more are put in series to increase the voltage of a given group (Pr.).

Evaporation[1] *and Salt Separation:*

The decomposition efficiency of the cells being in the range of only 50 per cent, about half of the NaCl charged is in the weak caustic and is recovered by reason of its low solubility in caustic soda solutions after concentration. Hence the weak or about 10 or 11 per cent NaOH solution is evaporated to around 50 per cent NaOH in a double- or triple-effect evaporator with salt separators, followed by a washing filter. The salt so recovered is made again into charging brine. In the evaporators, nickel tubes are usually used to lessen iron contamination. Sometimes even the evaporators are nickel lined to avoid this contamination and also caustic embrittlement of the steel. With the caustic soda liquor from the evaporator containing 50 per cent NaOH, it will dissolve only about 1 per cent of NaCl and other sodium salts after cooling. This liquor may be sold, after thorough settling, as liquid caustic soda in tank cars or drums. Indeed about half of the electrolytic caustic is so disposed of (Op.).

Final Evaporation:

Either the cooled and settled 50 per cent caustic or a specially purified caustic may be concentrated in a single-effect final or high evaporator to 70 or 75 per cent NaOH, using steam of 75 to 100 lb. gage. This very strong caustic must be handled in steam-jacketed pipes to prevent solidification. It is run to the finishing pots. Another method of dehydrating 50 per cent caustic utilizes the precipitation of sodium hydroxide monohydrate. This monohydrate contains less water than the original solution. The precipitation is accomplished by the addition of ammonia to the 50 per cent solution.[2] This also purifies the caustic.

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[1] See PERRY *op. cit.*, pp. 1041–1078 for general principles of heat transfer, salt separation, single- and multiple-effect evaporation, and necessary equipment involved in the concentration of caustic soda solutions. See p. 1600 for calculations of c.c.d. washing of the salt separated, and pp. 2102–2103 for materials of construction. A detailed study of the evaporation of cell liquor is presented on pp. 172–185 of Badger and Baker, *op. cit.*

[2] MACMULLIN, Concentration of Sodium Hydroxide, U.S. Pat., 1961590, June 5, 1934; MUSKAT, Concentration of Caustic, U.S. Pat., 2285300, June 2, 1942; MUSKAT and AYRES, Purification of Caustic, U.S. Pat., 2285299, June 2, 1942.

If the 50 per cent caustic is treated with anhydrous ammonia[1] particularly in countercurrent manner, there separate from the resulting aqua ammonia, free-flowing anhydrous crystals. Naturally this procedure should be carried out in pressure vessels (Pr.).

Finishing of Caustic in Pots:

Although 50 per cent caustic was at one time finished in cast-iron direct-fired pots, the heat efficiency is so low that good practice now handles only 70 or 75 per cent NaOH in this fashion. The final temperature is 500 to 600°C. and boils off all the water but about 1 per cent or less. These pots must be made of special close-grained cast iron. The hot anhydrous caustic is treated with sulfur to precipitate iron and settled. The product is pumped out by lowering, into the molten caustic, a centrifugal pump that discharges the caustic into thin steel drums holding about 700 lb. or to the flaking machine (Op.).

Special Purification of Caustic:

Some of the troublesome impurities in 50 per cent caustic are colloidal iron, sodium chloride, and sodium chlorate. The iron is often removed by treating the caustic with 1 per cent by weight of 300-mesh calcium carbonate and filtering the resulting mixture through a Vallez filter on a calcium carbonate precoat. The chloride and chlorate may be removed by allowing the 50 per cent caustic to drop through a column of 50 per cent aqueous ammonia solution. This treatment produces caustic almost as free of chlorides and chlorates as that made by the mercury process. To reduce the salt content of the caustic necessary for certain uses, it is cooled to 20°C. in equipment such as outlined in Fig. 5. However, another crystallization method used industrially involves the actual separation of the compound $NaOH \cdot 3\frac{1}{2}H_2O$ leaving the NaCl in the mother liquor.[2] A different procedure reduces the salt content of the caustic soda solution by formation of the slightly soluble complex salt $NaCl \cdot Na_2SO_4 \cdot NaOH$.[3] It should be noted that mercury cells furnish a caustic soda free from salt. These purification or manufacturing methods give a *high-grade* caustic with less than 1 per cent impurities (anhydrous basis). The *standard grade* contains 2½ to 3 per cent impurities (anhydrous basis) (Pr.).

Chlorine Drying:

The hot chlorine evolved from the anode carries much water vapor. It is first cooled to condense most of this vapor and then dried in a sulfuric acid scrubber or tower as shown in Fig. 5. Up to the sulfuric acid tower, the wet chlorine should be handled in stoneware, Duriron, or similar resistant material; after drying, iron or steel can be employed (Op. and Pr.).

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[1] MUSKAT, Method for Producing Anhydrous Caustic, U.S. Pat. 2196593, Apr. 9, 1940.

[2] HOOKER and MARSH, Purifying Caustic Soda, U.S. Pat. 1733879 (1929).

[3] HUBER, Removal of Salt from Caustic Soda Produced by Diaphragm Cells, *Can. Chem. Met.*, **17**, 52 (1933); *Chem. Abstracts*, **27**, 2384 (1933).

Chlorine Compression and Liquefaction:[1]

The dried chlorine is compressed to 35 lb. gage or sometimes as high as 80 lb. The usual type of compressor employed is the Nash Hytor (Fig. 6) constructed of iron and with concentrated sulfuric acid as the sealing liquid. The heat of compression is removed progressively by water and finally by refrigeration to about −20°F.; when all the chlorine must be liquefied, it is cooled to as low as −50°F. The liquid chlorine is stored and filled into either small cylinders or the ton cylinders, or the 50-ton tank cars that are shipped to large consumers. There is always some residual or "blow gas," this being the equilibrium mixture of chlorine and air. The blow gas is used to make chlorine derivatives, either organic or inorganic, especially bleaching powder (Op.).

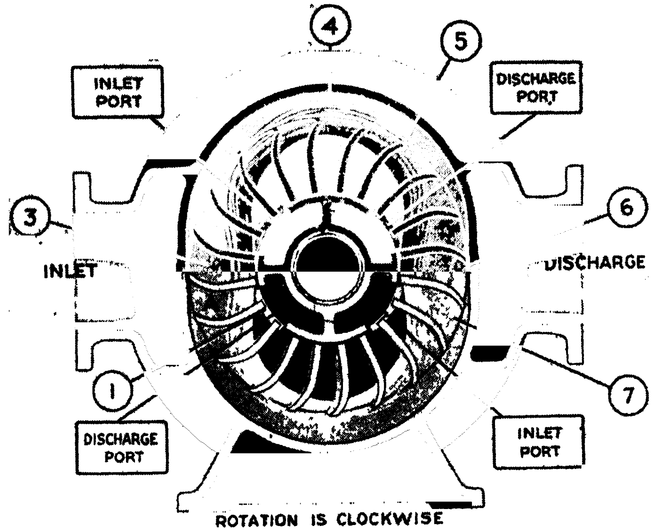

Fig. 6.—Nash Hytor pump. The rotor (5) revolves freely within the elliptical casing (6) containing a liquid which is usually water or sulfuric acid. The latter is used when the pump is on chlorine service. The liquid turning with the rotor is forced up against the casing (6) by centrifugal action and alternately recedes from (4) and is forced back into the rotor at (3) twice in a revolution. As the liquid recedes from the rotor, it draws the gas to be compressed through the inlet ports into the rotor by means of openings in the bottom of the rotor chambers. When the liquid is forced back into the rotor by the converging casing, the compressed gas is discharged through appropriate discharge ports at the bottom of the rotor chambers and out the pump discharge.

Hydrogen Disposal:

The hydrogen is very frequently made into other compounds such as hydrochloric acid or ammonia (see page 393) or employed for hydrogenations of organic compounds (Pr.).

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[1] Badger and Baker, *op. cit.*, pp. 188–191; *cf.* Perry, *op. cit.*, p. 1695; Magee, Liquid Chlorine Systems, *Chem. & Met. Eng.*, **50**, No. 8, 102 (1943).

Electrolytic Cells.[1]—The cells used in the United States may be divided into two general types: mercury cathode and diaphragm. Such a division takes into account the means of keeping apart the anode and cathode products. This separation is essential to prevent interaction of the primary products forming hypochlorites, which would greatly cut down the current efficiency of the cell, contaminate the caustic soda, and oxidize the anode carbon electrodes.

The mercury cell deposits the sodium in mercury as an amalgam. The mercury itself acts as the cathode, and the amalgam formed is decomposed in another compartment by water. These cells run at high current densities and have a current efficiency of about 95 per cent.[2] The caustic produced by these mercury cells results from the action of water on the mercury amalgam and, consequently, it is very pure and contains no chlorides. The caustic is from two to four times as strong as the 11 to 13 per cent produced from the diaphragm cells. The evaporation operation is thus cheapened.

The diaphragm cells contain a diaphragm of asbestos to separate the anode from the cathode. This allows ions to pass through by electrical migration but reduces diffusion of products. Diaphragms permit the construction of compact cells of lowered resistance because the electrodes can be placed close together. Because of their resistance, these cells require a higher voltage and a higher hydrostatic pressure on the brine feed. The diaphragms become clogged and must be replaced from every 100 to 200 days. The diaphragm permits a flow of brine from the anode to cathode and thus greatly lessens or prevents by-reactions such as would form sodium hypochlorite. In some of the cells the cathode compartment is "dry" and in others there is cathode liquor or kerosene, but in any case at a *lower head* than in the anode compartment, in order to ensure liquor movement from anode to cathode (see Fig. 7).

Castner Cell.—The Castner cell, as operated by Mathieson Alkali Works, is one of the most successful of the mercury cells. It consists of a concrete box 4 ft. long, 4 ft. wide, and 6 in. deep, which is divided into three compartments by partitions that extend to within 1/16 in. of the bottom. A layer of mercury as an intermediary cathode is on the bottom and separates yet connects the three compartments. In the outer compartments several T-shaped graphite anodes extend within an inch of the mercury. The inner compartment contains an iron grid which is the cathode. To start the cell, the two outer sections are filled with brine and the center division with water. The cell is pivoted at one end and rests on an eccentric at the other end, which rocks the mercury back and forth between the compartments about once every minute. Chlorine is liberated at the anodes and sodium forms an amalgam with the mercury. When the amalgam flows into the water compartment, the sodium reacts to give caustic soda and hydrogen.

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[1] *Cf.* PERRY, *op. cit.*, pp. 2791–2797, for cuts of various caustic cells and for a tabular comparison of operating results; MANTELL, "Industrial Electrochemistry," 2d ed., McGraw-Hill Book Company, Inc., New York, 1940.

[2] See PERRY, *op. cit.*, p. 2796, where current densities of two to three times those for diaphragm cells are given.

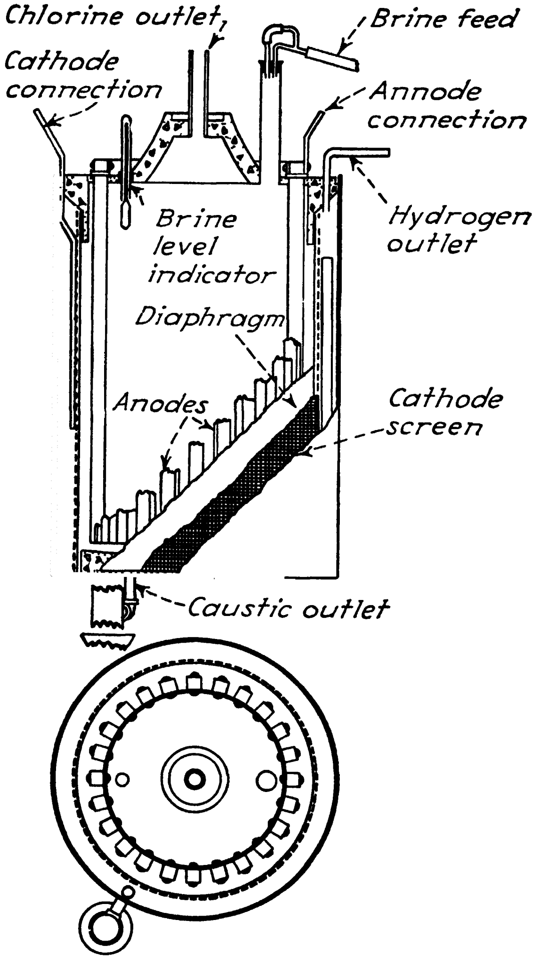

FIG. 7.—Vorce cell, elevation and cross section.

Salt is added continuously to the brine, and the caustic is drawn off when it reaches a desired concentration. Ten per cent of ~~the current~~ is shunted around the cathode compartment ~~to prevent oxidation of~~ the mercury to HgO. These cells are inexpensive in ~~construction except~~ for the capital invested in the ~~mercury~~ used—150 lb. per cell. The current at the anode is 630 amp. with a voltage of 4.3.

Vorce Cell.—This cell, which has a dry cathode compartment, is shown[1] in Fig. 7 and is one of the widely used chlorine cells at the present time. The over-all shape is cylindrical with dimensions of 26 in. in diameter and 42 in. in height. The cylinder is made of cement and ground asbestos surrounded by a steel container tank. Twenty-four Acheson graphite anodes extend down from the dome of the cell into the brine. The anodes are 2 by 2 in. in cross section and are fastened to a copper anode ring outside the cell. The cathode consists of a cylindrical steel screen. Attached to the screen and separating it from the anode solution is an asbestos diaphragm. The caustic liquor is discharged by gravity. In a plant the cells are operated with as many as 70 in series under a current of 1,000 amp. and 3.5 volts per cell.

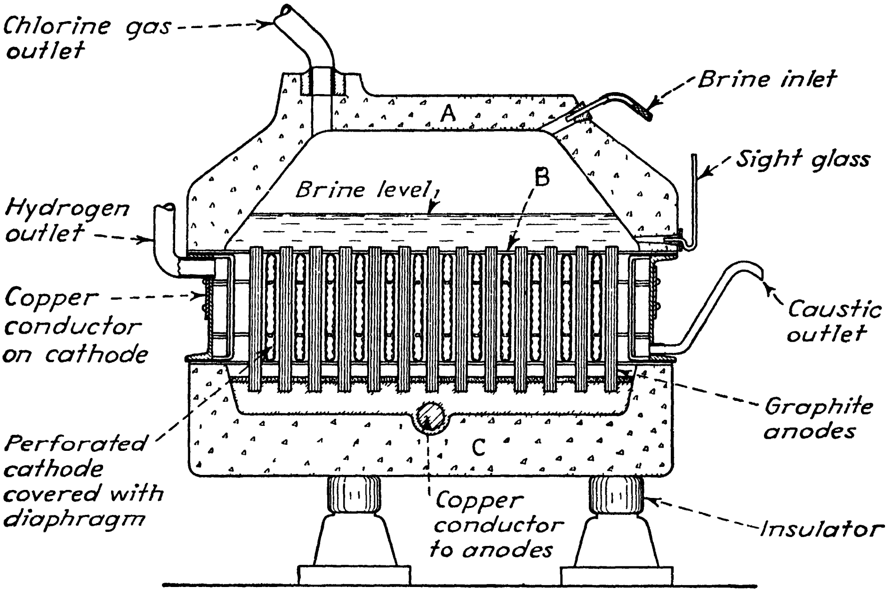

FIG. 8.—Elevation of Hooker S type cell.

Hooker S Cell.—One of the most recent advances in diaphragm cells was made with the introduction of the Hooker S cell.[2] It is rectangular or roughly cubical in type but is built so as to conserve space. The anodes are graphite plates which project upward from a lead slab and between finger-type cathodes made from crimped steel wire. This cathode is directly covered with asbestos and forms the diaphragm which is completely submerged. The outside is constructed of concrete on a steel frame, heavily insulated to conserve heat since the cell operates at a higher temperature than most cells. An elevation of this cell is depicted in Fig. 8.

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[1] See also PERRY, *op. cit.*, pp. 2791–2797, for this and other cells.

[2] U.S. Pats., 1866065; 1865152; 1862244; 1862245; STUART, HYSTER, and MURRAY, *Chem. & Met. Eng.*, **45**, 354 (1938).

The operating temperature of the Hooker S cell is about 85°C., much higher than the other cells (60 to 70°C.). Its voltage is about 3.4 with a voltage efficiency of 65 per cent; the amperage is 7,000 with an amperage efficiency of 95 per cent. The high operating temperature contributes to the voltage efficiency as there is less resistance to current flow at this temperature. But, if the temperature is too high, the products attack the cell wall too fast. Figure 9 represents a typical installation.

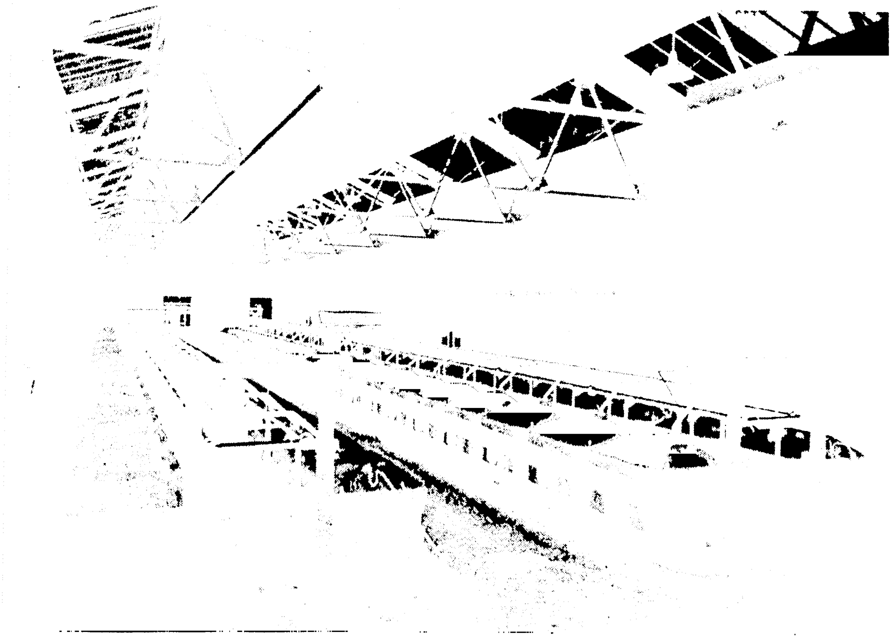

FIG. 9.—Typical Hooker S type cell installation.

There are several other cells in operation at various plants, mostly of the rectangular type. The *Nelson* cell has an asbestos diaphragm and a U-shaped steel cathode throughout its length. The *Allen-Moore*, the *Buck-McRae*, and the *Hargreaves-Bird* cells are described in outline in Perry, *loc. cit.* The only others of importance are the *Gibbs* and the *Wheeler* cells which are cylindrical and resemble the Vorce cell.

A new method for the production of chlorine through *nitrosyl chloride*[1] is in operation at Hopewell, Va. Common salt is treated with nitric acid to form sodium nitrate, a valuable fertilizer, and chlorine.

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[1] DEJAHN, Is There a Profit in Chlorine and Nitrate from Salt? *Chem. & Met. Eng.*, **42**, 537 (1935).

The reactions may be simplified as follows:

$$3NaCl + 4HNO_3 \rightarrow 3NaNO_3 + Cl_2 + NOCl + 2H_2O$$
$$2NOCl + 3HNO_2 + 3O_2 + H_2O \rightarrow 5HNO_3 + Cl_2$$

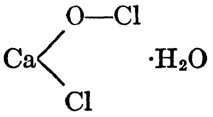
The advantage of this process is that it furnishes another method for making chlorine. Forty tons per day were being produced by this process in 1944.

BLEACHING POWDER

A decreasing tonnage of chlorine goes into the production of bleaching powder largely because of its instability and the large proportion of inert material. The reaction by which bleaching powder is made is

$$Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 + H_2O$$

The correct formula is



This reaction is carried out below 50°C. in a countercurrent fashion by passing chlorine through a rotating steel cylinder with inner lifting blades which shower the solid in the path of the gas. When allowed to stand in the air, the bleaching powder absorbs carbon dioxide. (Other inorganic acids will also liberate the HOCl.)

$$2CaCl(OCl) + CO_2 + H_2O \rightarrow CaCl_2 + CaCO_3 + 2HClO$$
$$2HClO \rightarrow 2HCl + O_2$$

However, simply on standing, the following decomposition takes place:

$$2CaOCl_2 \rightarrow 2CaCl_2 + O_2$$

When dissolved in water, the reaction gives ionized calcium chloride and hypochorite.

$$2CaCl(OCl) \rightarrow Ca^{++} + 2Cl^- + Ca^{++} + 2OCl^-$$

The OCl^- ion decomposes, liberating oxygen. We say that, in general, bleaching powder is an oxidizing agent. However, its activity is measured in what is termed *available chlorine*, which is, by definition, the same weight as that of gaseous or liquid chlorine that would exert the same action as the chlorine compound in question. In case of bleaching powder, $CaOCl_2$, the available chlorine is the same as the percentage of chlorine, but in case of calcium hypochlorite, $Ca(OCl)_2$, the available chlorine is twice the percentage (49.6) of chlorine in $Ca(OCl)_2$ or 99.2 per cent. This is another way of saying that 1 mole of Cl_2 is equivalent in oxidizing power to 1 mole of HOCl, or to the ion OCl^-. Bleaching powder by this convention contains about 35 or less per cent of available chlorine when freshly manufactured. The available chlorine concept may be further explained by the reactions:

For calcium hypochlorite:

$$Ca(OCl)_2 + 2HCl \rightarrow CaCl_2 + 2HOCl$$

or

$$Ca(OCl)_2 \rightarrow Ca^{++} + 2OCl^-$$

One mole of bleaching powder will furnish only half this amount of OCl^- ions.

For chlorine:

$$Cl_2 + H_2O \rightarrow HOCl + HCl$$

Calcium hypochlorite, $Ca(OCl)_2$, itself may be made in several ways. One method that has been used is the chlorination of calcium hydroxide as in the manufacture of bleaching powder, followed by the separation of the calcium hypochlorite through salting out from solution with sodium chloride. Another method of manufacture is by the formation under refrigeration of the salt, $Ca(OCl)_2 \cdot NaOCl \cdot NaCl \cdot 12H_2O$,[1] which is prepared by the chlorination of a mixture of sodium and calcium hydroxides. This is reacted with a chlorinated lime slurry, filtered to remove salt, and dried, resulting finally in a stable product containing 65 to 70 per cent $Ca(OCl)_2$. The final reaction is

$$2[Ca(OCl)_2 \cdot NaOCl \cdot NaCl \cdot 12H_2O] + CaCl_2 + Ca(OCl)_2 \rightarrow 4Ca(OCl)_2 \cdot 2H_2O + 4NaCl + 16H_2O$$

The great advantage in calcium hypochlorite is that it does not decompose on standing as does bleaching powder. It is also twice as strong as ordinary bleaching powder, and it is not hygroscopic.

SODIUM HYPOCHLORITE

Sodium hypochlorite is employed as a disinfectant and deodorant in dairies, creameries, water supplies, sewage disposal, and for household purposes. It is also used as a bleach in laundries. During the First World War, it was employed for treatment of wounds as a stabilized isotonic solution. As a bleaching agent, it is very useful on cotton, linen, jute, artificial silk, paper pulp, and oranges. Indeed much of the chlorine bought for bleaching cellulose products is converted into sodium hypochlorite before use. The most common method for making it is the treatment of sodium hydroxide solution with gaseous chlorine.

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[1] MacMullin and Taylor, U.S. Pat., 1787048 (1930). See Rogers' "Manual of Industrial Chemistry," 6th ed., D. Van Nostrand Company, Inc., New York, 1942, on pp. 453, 454 for other methods.

$$Cl_2 + 2NaOH \rightarrow NaCl + H_2O + NaOCl$$

The other once widely used method was the electrolysis of a concentrated salt solution wherein the same product was made. These electrolytic cells do not have any diaphragm and are operated at high current density in nearly neutral solution. The cells are designed to function at a low temperature and to bring the cathode caustic soda solution in contact with the chlorine given off at the anode.

SODIUM CHLORITE

Sodium chlorite has been introduced recently by the Mathieson Alkali Works. Its formula is $NaClO_2$, and the 80 per cent commercial material has about 125 per cent "available chlorine." It is manufactured[1] from chlorine through calcium chlorate to chlorine dioxide, ending with the reaction:

$$4NaOH + Ca(OH)_2 + C + 4ClO_2 \rightarrow 4NaClO_2 + CaCO_3 + 3H_2O$$

Sodium chlorite is a powerful but stable oxidizing agent. It is capable of bleaching much of the coloration in cellulosic materials without tendering the cellulose. Hence it finds use in the pulp and textile industries, particularly in the final whitening of kraft paper. It is also more rapid in vat dyeing[2] than sodium dichromate and does not dull the shade.

Problems

1. A plant is to manufacture 500,000 lb. of Solvay ammonia soda per day, containing 96.7 per cent Na_2CO_3. How much salt will be required for the actual conversion if it is 98.5 per cent NaCl? If the carbonating towers consume only 66 per cent of the salt, how much salt is actually required?

2. A plant is making soda with a 98.1 per cent purity; 50,000 lb. of salt is actually converted. The reaction $NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$ goes 80 per cent to completion while the conversion of bicarbonate to carbonate is done without loss. How many pounds of $NaHCO_3$ (dry) are produced? How many pounds of dry soda ash are made? How much salt is originally used?

3. Calculate the weight of NaCl and of $CaCO_3$ to make 1 ton of soda ash containing the equivalent of 58 per cent Na_2O. Assume that 25 per cent excess NaCl is necessary in the first step and 7 per cent $NaHCO_3$ lost in washing.

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[1] TAYLOR, WHITE, VINCENT, and CUNNINGHAM, Sodium Chlorite, Properties and Reactions, *Ind. Eng. Chem.*, **32**, 899, (1940); FURNAS, "Rogers' Manual of Industrial Chemistry," *op. cit.*, p. 456.

[2] DUBEAU, FENRICH, and VINCENT, Reducing Time of Vat Dyeing with Textone, *Am. Dyestuff Reptr.*, **32**, 175, (1943); TAYLOR, WHITE, VINCENT, and CUNNINGHAM, *op. cit.;* TAYLOR and VINCENT, Chemistry of Chlorites, *Ind. Eng. Chem.*, **34**, 782 (1942).

4. 3,000 lb. of NaCl is to be converted into Na_2CO_3 per cycle by the Solvay process. Assume all reactions go 100 per cent and that 19 per cent of the salt put in is lost. 920 lb. of CO_2 is recirculated with losses of CO_2 amounting to 5 per cent of the total CO_2 present each cycle plus 10 per cent of the recycled CO_2. Ammonia losses are 0.5 per cent and the rest of the ammonia is recycled. Calculate the amounts of $CaCO_3$ and NH_3 that must be supplied initially for conversion of 3,000 lb. NaCl per cycle and that which must be supplied for each subsequent 3,000-lb. cycle.

5. A single-effect evaporator is to be designed to concentrate 250 gal. of 10 per cent NaOH solution (sp. gr. = 1.116) per hour to 50 per cent (sp. gr. = 1.540). Feed is to enter at 70°F. (steam pressure = 5 lb. per sq. in. gage). Vacuum is 27 in. referred to a 30-in. barometer. The specific heat of feed is 0.95; of finished liquor, 0.85.

Boiling point rise (50 per cent NaOH solution) = 30°F
Over-all heat transfer coefficient = 225.

The finished liquor will leave the evaporator at the boiling temperature and condensate will leave the basket at equilibrium temperature for 5 lb. steam. Calculate,

a. Area of heating surface to be supplied (sq. ft.).
b. Steam consumption in pounds per hour.
c. Expected steam economy.

6. Sodium carbonate crystals (decahydrate) are dissolved in 103 lb. of water. This is treated with a $Ca(OH)_2$ slurry giving 200 lb. of 9 per cent NaOH solution with a 92 per cent conversion. Calculate,

a. Weight of $Ca(OH)_2$ slurry.
b. Weight of $Na_2CO_3{\cdot}10H_2O$ used.
c. Percentage of Na_2CO_3 in NaOH solution.
d. Percentage of Na_2CO_3 solution.

7. A soda ash solution containing 22 per cent Na_2CO_3 is to be treated with lime (83 per cent conversion) to form a caustic solution containing 14 per cent NaOH. If there were 9.8 lb. of lime in the original suspension, what percentage of the total suspension is lime?

8. A caustic soda solution is to be made by adding a 16 per cent Na_2CO_3 solution in the proper stoichiometric proportions to a slurry containing 30 per cent $Ca(OH)_2$. If the conversion is 90 per cent complete, what is the concentration of the resulting solution?

9. A plant causticizes 300 tons of 95 per cent soda ash per day obtaining a 96 per cent yield. The lime is 96 per cent CaO and is used in theoretical amount. If 42 per cent NaOH liquor is to be made, how much lime is to be used and how much caustic soda will be produced daily?

10. The liquor from a diaphragm cell contains 10 per cent NaOH and 13 per cent NaCl. 15,000 lb. of caustic containing 2.3 per cent NaCl is produced per day by evaporation of the liquors. Calculate the pounds of salt that precipitate per day in the evaporators and the decomposition efficiency of the cell.

11. Chlorine gas and caustic are being made in Hooker-type cells. The chlorine contains 0.9 per cent oxygen and, for the purpose of measuring the rate of generation, more O_2 gas is added to the chlorine at a rate of 2 lb. O_2 per min. The gas now analyzes 3.0 per cent O_2. How much caustic (100 per cent) will be produced in one hour? (Temperature is 25°C., barometer normal.)

12. An alkali chlorine manufacturer has an excess of moist cell gas (97 per cent chlorine which he proposes to liquefy.

a. Draw a schematic diagram of the equipment required.

b. Describe the function of each unit and specify the material from which it may be constructed.

c. Describe the type of compression and liquefaction equipment you would select.

13. A battery of 50 Nelson cells produces 8 tons of Cl_2 per day. Cathodic current efficiency is 94 per cent. Anodic current efficiency is the same.

Calculate,

a. Amount of caustic soda produced in the cell per day.

b. Assuming 100 per cent current efficiency, calculate current in ampere-hours that passes through the cell if 1 amp.-hr. is required for 0.0033 lb. of NaOH.

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CHAPTER XVI

ELECTROLYTIC INDUSTRIES

Electrical energy is extensively consumed by the chemical process industries not only to furnish power through electrical motors but to give rise to elevated temperatures and directly to cause chemical change. Energy in the form of electricity causes chemical reactions to take place in the electrolytic industries presented in this chapter. The heat produced thereby is the basis for the high temperature required in the electrothermal industries, which will be discussed in Chap. XVII. Most of the electrolytic processes have been developed within the past 30 years and few of them are older than 60 years. The materials manufactured by the aid of electricity vary from chemicals that are also produced by other methods, such as caustic soda, hydrogen, and magnesium, to chemicals that at present cannot be made economically in any other way, such as aluminum and calcium carbide. See Table 2 for chemicals and metals made electrochemically.

TABLE 1.—TYPICAL POWER COSTS FROM WATER POWER EXCEPT WHERE OTHERWISE NOTED[a]

	Cents per Kw.-hr.
New York Harbor (steam)	0.67–1.3
Norway	0.1 –1.5
Sweden	0.1 –1.5
England	0.4 –0.5
Germany (brown coal)	0.38
Niagara Falls	0.3 up
Tennessee (steam)	0.38–0.6
Ontario, Canada	0.15–0.4

[a] PERRY, *op. cit.;* p. 2829, abridged.

The cost of electrical power is usually the deciding factor in the electrochemical industries. Thus, these industries have tended to become established in regions of cheap electrical power based on falling water, as at Niagara Falls and in Norway. The recent establishment of new areas of abundant and inexpensive electricity in the West and Northwest points the way to the growth of electrochemical industries in those regions. Typical power costs in various parts of the United States and other countries are given in Table 1, while Table 2 lists the kilowatt-hours needed to produce 1 lb. of the various materials.

TABLE 2.—CHEMICALS AND METALS MADE ELECTROCHEMICALLY[a]

Material	Process	Kw-hr per lb	Voltage per cell or furnace	Yearly kw-hr consumed
Alumina, fused	Electrothermal fusion	1–1.5	100–110	Large
Aluminum	Electrolytic reduction of alumina to aluminum	9.5–12.5	5.5–7	Very large
Ammonia, synthetic	Electrolytic hydrogen pressure hydrogenation	6.5		Large
Cadmium	Electrolytic precipitation of zinc lead residues	1–1.5	2.6	Small
Calcium	Electrothermal reduction			Small
Calcium carbide	Electrothermal reduction	1.3–1.6		Very large
Calcium cyanamid	Electrothermal reduction	1.4		Large
Carbon bisulfide	Electrothermal reaction	0.4–0.5	60	Large
Caustic soda chlorine	Electrolysis of brine	1.1–1.5	3.4–4.3	Very large
Copper	Copper electrowinning	0.8–1.3		Large
Copper	Electrolytic refining	0.07–0.16	0.18–0.4	Very large
Ferrochromium, 70%	Electrothermal smelting	2–3	90–120	Large
Ferromanganese, 80%	Electrothermal reduction	1.5–3	90–115	Very small
Ferromolybdenum, 50%	Electrothermal smelting	3–4	50–150	Small
Ferrosilicon, 50%	Electrothermal smelting	2–3.5	75–150	Very large
Ferrotungsten, 70%	Electrothermal smelting and refining	1.5–2	90–120	Small
Ferrouranium	Electrothermal smelting	3–5		Very small
Ferrovanadium, 30–35%	Electrothermal smelting	3.4	150–250	Small
Gold	Electrolytic refining	0.13	1.3–1.6	Very small
Graphite	Electrothermal change	1.5–2	80–200	Large
Hydrogen and oxygen	Electrolysis of alkalized water	140[b]		Small
Hypochlorite	Electrolysis of salt solution with mixing			Medium
Iron	Reduction in arc furnace	1–1.25		None
Iron castings	Electric melting duplex system continuous	 0.07 0.225		 Very small
Iron, sponge	Electrothermal low-temperature reduction	0.2		Very small
Lead	Electrolytic refining	0.94–0.05	0.35–0.6	Small
Magnesium, metallic	Electrolysis of magnesium chloride	8–13	6–9	Very large
Phosphoric acid	Electrothermal reduction to phosphorus, oxidation	2.7		Large

TABLE 2.—CHEMICALS AND METALS MADE ELECTROCHEMICALLY.[a]—(*Continued*)

Material	Process	Kw.-hr. per lb.	Voltage per cell or furnace	Yearly kw.-hr. consumed
Phosphorus	Electrothermal reduction	4.5	....	Large
Potassium chlorate	Electrolysis of potassium chloride solution (mixing)	3	....	Small
Potassium hydroxide	Electrolysis of potassium chloride solution	1–1.2	....	Small
Quartz, fused	Electrothermal fusion	5–8	....	Small
Silicon	Electrothermal reduction	6	....	Small
Silicon carbide	Electrothermal reduction	4.0–4.5	75–230	Large
Silver	Electrolytic refining	0.15–0.37	2.7–3.5	Very small
Sodium, metallic	Electrolysis of fused sodium chloride	7	....	Large
Sodium chlorate	Electrolysis of sodium chloride solution (mixing)	2.55–13.0	2.8–3.5	Small
Steel castings	Electric melting cold charge	0.25–0.38	....	Large
Steel ingot	Electric melting or refining or superrefining of molten charge	0.1	....	Large
Zinc	Electrolytic precipitation	1.1–1.6	3.5–3.7	Very large

[a] Based on House Document 103, 73d Congress, as reported in *Chem. & Met. Eng.*, **44**, 539 (1937) and supplemented by Mantell's tabulation in Perry, *op. cit.*, p. 2829.

[b] Kw.-hr. per M cu. ft.

Landis writes,[1] "The electrochemical process has completely *revolutionized* the production of certain primary products and at such *lowered cost* as to permit the development of new secondary industries utilizing these cheaper raw materials." Examples of such lowered costs are for chlorine and sodium and hydrogen peroxide, as well as for aluminum.

Direct current is used in the electrochemical industries. Most of this direct current (73 per cent) is produced by mercury arc rectifiers[2] although a recent development is the use of direct-current generators.[1] These generators are actuated by gas engines, and the cost of the current in regions of low-priced gas is said to be very economical.

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[1] FURNAS, editor, "Rogers' Manual of Industrial Chemistry," 6th ed., p. 479, D. Van Nostrand Company, Inc., New York, 1942. Italics in quotation are by Shreve.

[2] RHEA, 1942 Electrical Developments in the Chemical Industry, *Chem. Eng. News*, **21**, 90 (1943).

ALUMINUM

Aluminum is potentially the most abundant metal in the world. It makes up 7.50 per cent of the known terrestrial matter. Every country possesses large supplies of aluminum-containing materials, but as yet processes for obtaining metallic aluminum from most of these compounds are not economical.

History.—Although Wohler is usually credited with the first production of metallic aluminum in 1827, the first obtaining of this metal was in 1825 by Oersted, a Dane. He heated aluminum chloride with a potassium-mercury amalgam. In 1845 Henri Sainte-Claire Deville produced globules of aluminum from a fused sodium-aluminum chloride bath. This process was operated for about 35 years and the metal sold for $100 a pound. By 1886 the price had been reduced to $8 a pound, chiefly by reason of the use of cryolite as a flux in the bath, the lowered cost of the metallic sodium needed for the reduction, and the improvements in the equipment.

Large-scale manufacture of aluminum was not achieved until the advent of the Hall process. In 1886, Charles Hall produced the first aluminum by the present-day process: electrolysis of alumina dissolved in a fused bath. The same year Paul Héroult was granted a French patent for a process similar to that of Hall. He was not able to obtain a United States patent, however, as Hall's patents were granted the priority.[2] By 1893, the production of aluminum had increased so rapidly by Hall's procedure that the price had fallen to $2 per lb. The industry grew steadily, based soundly on new and expanding markets, created largely by its own study of the properties of aluminum and of the avenues for economic consumption of this new metal. With this growth in manufacture came a decrease in cost which the Aluminum Company of America largely passed on to its customers, even reducing the price first to 17 cents per lb. and then to 15 cents per lb. (1943) during the first year of the Second World War.

Economics and Uses.—Before the war the United States produced 33 per cent of the world's supply of aluminum.[3] In 1939 the United States produced approximately 323,000,000 lb. of metallic aluminum.

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[1] JOLLY, The Recent Expansion of the Aluminum Industry, *Science*, **96**, No. 2480, 29 (1942).

[2] VAN DOREN, Studies in Chemical Patent Procedure, *Ind. Eng. Chem.*, **21**, 120 (1929).

[3] "Minerals Yearbook," 1938, p. 577.

The advent of war has caused a tremendous increase in the demand for the metal, and it is estimated that at the end of 1943 the United States production approached 2,000,000,000 lb., or 6½ times the 1939 production.[1] Table 3 shows the distribution of aluminum among the various industries in 1936. During the war, almost the entire production entered into the construction of airplanes and other military articles.

TABLE 3.—DISTRIBUTION OF ALUMINUM IN THE UNITED STATES IN 1936

Industry	Per Cent
Transportation (land, air, and water)	20
Machinery	18
Cooking utensils	13
Miscellaneous foundry and metalworking	13
Electrical conductors	12
Iron and steel metallurgy	5
Chemical	3
Building	3
Food products and miscellaneous	13

The unusual combination of lightness and strength makes aluminum applicable for many uses that other metals cannot fill. Weight for weight, aluminum has twice the conductivity of copper, and it also has a high ductility at elevated temperatures. Aluminum may be alloyed with other metals, such as copper, magnesium, beryllium, and manganese, and thus have its usefulness increased.[2] Metallic aluminum or aluminum alloys are employed for structural shapes for aircraft, automobiles, trucks, and railway cars, for electrical conductors, for cast and forged structural parts.

Manufacture.—Metallic aluminum is produced by the electrolytic reduction of pure alumina in a bath of fused cryolite. The production of the pure alumina will be discussed in Chap. XXI.[3] It is not possible to reduce alumina with carbon because at the temperature required for this reduction the aluminum comes off as a vapor and is carried away with the carbon monoxide. This metallic vapor cannot be condensed by cooling because the reaction reverses at lower temperatures and thus converts the aluminum back to alumina. The *energy change* involved in the reaction

$$Al_2O_3 + 1\tfrac{1}{2}C \rightarrow 2Al + 1\tfrac{1}{2}CO_2; \qquad \Delta H = +235{,}000 \text{ cal.}^4$$

amounts *practically* to around 10 kw.-hr. per lb. Consequently this metal cannot be made economically unless low-priced electrical energy is available. The carbon for the reaction comes from the anode, for which is required from 0.6 to 0.7 lb. of carbon per pound of metal. The carbon dioxide evolved contains from 10 to 50 per cent carbon monoxide.

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[1] JOLLY, *op. cit.*

[2] FRARY, The Aluminum Industry, *Chem. Eng. News*, **20**, 1646 (1942); FRARY, Economics of Aluminum Industry, *Ind. Eng. Chem.*, **28**, 146 (1936).

[3] "Making Alumina," pictured flow sheet, *Chem. & Met. Eng.*, **47**, 707 (1940).

[4] Some CO is formed. This reaction requires more energy.

The *unit operations* (Op.) and *unit processes* (Pr.) involved in the production of metallic aluminum are as follows:

The cryolite bath is prepared (Pr.).

Alumina is dissolved in the molten cryolite bath (Op.).

The molten solution of alumina in cryolite is electrolyzed to form metallic aluminum (Pr.).

The carbon electrode is oxidized by the oxygen liberated (Pr.).

The molten aluminum is tapped off and cooled (Op.).

The cells used for the reduction are made of iron, lined with firebrick, and covered with carbon to conduct the current,[1] as depicted in Fig. 1.

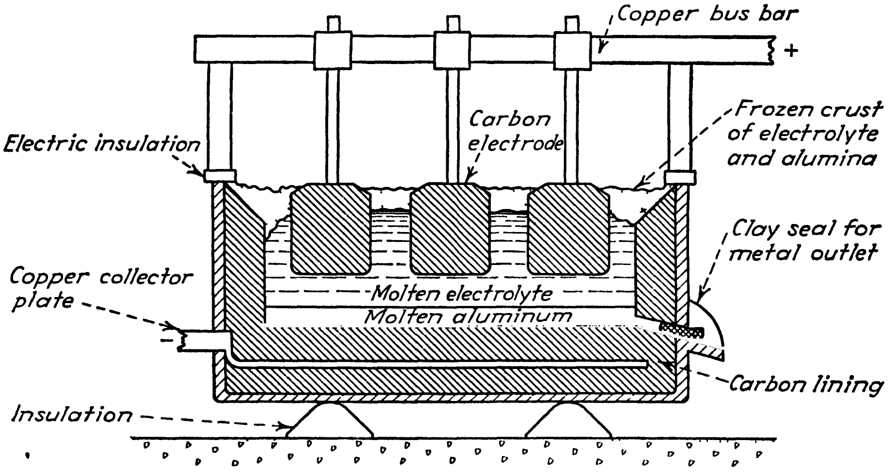

FIG. 1.—Electrolytic aluminum cell.

The anodes are made from hard and pure carbon obtained from petroleum coke and extend to within about 2 in. of the molten aluminum in the bottom of the cell. As they are gradually consumed by the oxygen liberated, they are hung from an overhead bar so that they may be lowered as needed. Any impurities in the anodes would be liable to contaminate the metal. The molten aluminum metal that gathers on the bottom serves as the cathode for the cell. The bottom of the cell is slanted to permit the metal to be tapped off daily.

The "solvent" for the alumina is fused cryolite, $AlF_3 \cdot 3NaF$, obtained from Greenland or manufactured synthetically by the action of hydrofluoric acid on aluminum hydroxide in the presence of soda. Fluorspar is introduced into the bath to lower the melting point. The average bath has the following approximate composition: $2AlF_3 \cdot 6NaF \cdot 3CaF_2$. The alumina to be reduced is added to the molten cryolite at such intervals as to maintain a 2 to 6 per cent dissolved alumina content in the bath at all times.

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[1] JEFFRIES, Aluminum from Chemical Element to an Industrial Metal, *Iron Age*, **137**, No. 8, 22 (1936); LEE, Three Plants in One, *Chem. & Met. Eng.*, **50**, No. 5, 145 (1943).

If the level of the bath falls below the point where the electrolyte is in full contact with the anodes, the resistance of the cell increases, causing a signal lamp shunted across the cell to increase in brightness. Additional alumina is then stirred in. The melted cryolite is covered with a blanket of alumina which rests on a crust of frozen electrolyte. This alumina is thus preheated before being dissolved in the bath. The carbon dioxide and monoxide by-products are vented off through hoods.

The tendency for the aluminum metal formed to sink to the bottom of the cell is the result of careful control of the density of the various layers of the bath. At the temperature of electrolysis, 900 to 1000°C., the specific gravities of the various layers are as follows: alumina in cryolite, 2.095; molten aluminum, 2.29.[1] The aluminum, being heavier, can thus be easily tapped off the bottom of the cell.

The theoretical voltage for reduction of the alumina is 2.0 volts, but in actual practice, 5.5 to 7 volts are necessary per cell. The cells are connected in series of 30 to 100, and the amperage of each cell is 8,000 to 30,000. The more current that can be used in a cell, the lower the cost of producing the aluminum as the labor is about the same. However, because of mechanical and handling difficulties, cells of larger than 30,000 amp. are not practicable. A furnace 8 by 4 by 4 ft. produces about 120 lb. of aluminum per day. The energy consumption is 9.5 to 12 kw.-hr. per lb. of aluminum.

For electrical establishments such as those manufacturing aluminum, large tonnages of copper are ordinarily required for bus bars, electrical wiring, motors, and other such demands. During the national emergency of the Second World War, the silver ordinarily stored in the vaults at West Point was lent to the extent of thousands of tons to lessen demands for copper. For the expansion plants of the Aluminum Company of America alone,[2] 13,000 tons of silver were so lent and were employed for heavy bus bars.

Aluminum is refined electrolytically. A copper-aluminum alloy in contact with carbon forms the anode of the cell, the cathode is purified molten aluminum, and the electrolyte is a layer of fused cryolite, aluminum fluoride, and barium fluoride. The pure aluminum is dissolved from the anode and deposited on the cathode.[1] The purity of this aluminum is 99.80 to 99.90 per cent. The highly refined aluminum *is appreciably softer than ordinary aluminum. Many alloys*[2] *of aluminum are employed to give greater strength or hardness.* These are important because of their pleasing appearance, corrosion resistance, and strength per unit of weight. The latter property makes aluminum and its alloys of the utmost necessity for the manufacture of airplanes.

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[1] PERRY, *op. cit.*, p. 2798. Operating data are tabulated.

[2] JOLLY, *op. cit.*, p. 31.

MAGNESIUM

Magnesium is a very light silvery white metal which only recently has achieved widespread industrial use. Magnesium does not occur free in nature, but its compounds are abundant as magnesium is the eighth element in order of occurrence in the world. The raw materials are also widely distributed throughout the globe, particularly as sea water is a practical and very important source for magnesium compounds. Hence there need never be any shortage of the economical raw materials for magnesium metal and most of its salts. Magnesium salts are presented in Chap. XI.

History.—Although metallic magnesium was first isolated by Bussy in 1829, its existence was discovered by Davy in 1808. Uses for this metal were slow in being developed. As late as 1918 almost all of the magnesium produced was used for flashlight powder, although during the First World War part of the production was consumed in pyrotechnics. The United States output in 1918 was only 284,118 lb. and this quantity dropped sharply as soon as the war was over.[3] During the next 15 years intensive research brought forth many new uses for magnesium. By 1930 it was being fabricated into complicated castings, sheets, and forgings, and a method of welding it was also perfected. Extremely lightweight, strong magnesium alloys of great importance to the aircraft industry were developed during the period 1930–1940.[4] The demands of the Second World War for better and lighter airplanes were met by these light magnesium alloys. Consequently magnesium production was expanded tremendously to meet this new demand and also to supply the material for incendiary bombs. Representative magnesium

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[1] Frary, Electrolytic Refining of Aluminum, *Trans. Am. Electrochem. Soc.*, **47**, 275 (1925); Edwards, Contributions of Aluminum to Metallurgical Progress, *Metal Progress*, **29**, 34 (1936).

[2] Perry, *op. cit.*, pp. 2124, 2137, tabulates such alloys.

[3] Killeffer, Magnesium from the Sea, *Ind. Eng. Chem.*, *News Ed.*, **19**, 1189 (1941).

[4] For an extensive review of the corrosion-resistant properties of magnesium-aluminum alloys, see Benson and Mears, Aluminum-Magnesium Alloys Resist Attack, *Chem. & Met. Eng.*, **49**, No. 1, 88 (1942).

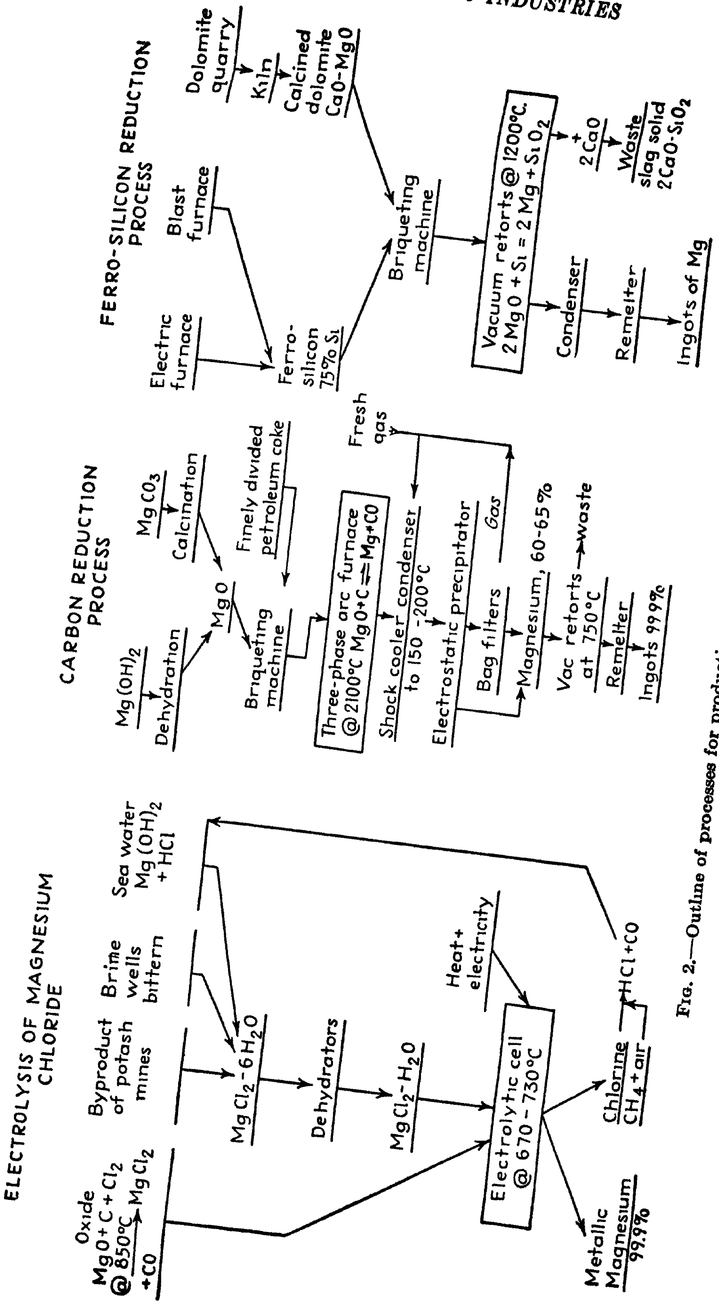

FIG. 2.—Outline of processes for production of metallic magnesium.

alloys are Dowmetal H: Al, 6.5 per cent; Mn, 0.2 per cent; Zn, 3.0 per cent; Mg, rest; and Dowmetal M: Mn, 1.5 per cent, with Mg rest.

Uses and Economics.—The primary use for magnesium is in the production of the lightweight structural alloys just mentioned, although in wartime incendiary bombs, flashlight powder, and flares consume a large part of the supply. At present all of the magnesium produced is being demanded for military purposes but, when this need is past, many new applications for this metal surely will be found.

The production of magnesium in the United States in 1941 was approximately 60,000,000 lb., but production has been expanded so rapidly that it is estimated that between 200,000,000 and 250,000,000 lb. was produced in 1943. As usual in the development of a material from a relative rarity to a tonnage article, the price of magnesium has dropped from $1.81 per lb. in 1918[1] to 20½ cents per lb. in 1943.

Manufacture.—Three processes at least are technically important for the production of metallic magnesium. Figure 2 depicts simplified flow sequences for these. Only one of these processes (magnesium from magnesium chloride) is an electrolytic process, but for comparison the other two will be discussed briefly in this chapter. Other procedures have been considered, such as the reduction of magnesia by calcium carbide:

$$\mathrm{MgO} + \mathrm{CaC_2} \xrightarrow{1150°\mathrm{C.}} \mathrm{Mg} + \mathrm{CaO} + 2\mathrm{C}$$

Pressed briquettes made from magnesium oxide and calcium carbide are reacted in an electric furnace at 1150°C. and 0.3 mm. absolute pressure, with a conversion of 75 to 80 per cent over 6 hr.

Electrolysis of Magnesium Chloride.—Magnesium chloride for the production of magnesium is obtained in a number of ways: from salines,[2] from brine wells, from the reaction of magnesium hydroxide (from sea water or dolomite) with hydrochloric acid, and from the reaction of magnesium oxide with carbon and chlorine. The pioneer producer, the Dow Chemical Company, manufactures magnesium from magnesium chloride obtained from brine wells and sea water. Basic Magnesium, Inc., at Las Vegas, Nev., produces magnesium from the chloride made by treating magnesium oxide with carbon and chlorine.

The raw materials for the preparation of magnesium chloride from sea water are oyster shells and sea water. The oyster shells, which are almost pure calcium carbonate, are burned to lime, slaked, and mixed with the sea water thus precipitating magnesium hydroxide (*cf.* Fig. 3

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[1] DOERNER, Present Outlook for a Magnesium Industry in the Northwest, *Wash. Min. Exp. Sta. Bull. P*, Pullman, Wash., 1937.

[2] MANNING and KIRKPATRICK, Better Utilization of Mineral Resources through New Chemical Technology, *Chem. & Met. Eng.*, **51**, No. 5, 92 (1944).

and Chap. XI). *This magnesium hydroxide is filtered off and treated* with hydrochloric acid, forming a magnesium chloride solution which is evaporated enough to cause any small amounts of sodium chloride and other impurities to crystallize out. These salts are removed by filtration and the concentrated magnesium chloride solution is evaporated[1] to $MgCl_2 \cdot 6H_2O$. This salt dehydrates easily to $MgCl_2 \cdot 2H_2O$, which may be heated in an atmosphere of either HCl or NH_4Cl to produce anhydrous $MgCl_2$. However, the almost dehydrated salt can have the last water driven off in the electrolytic cell.

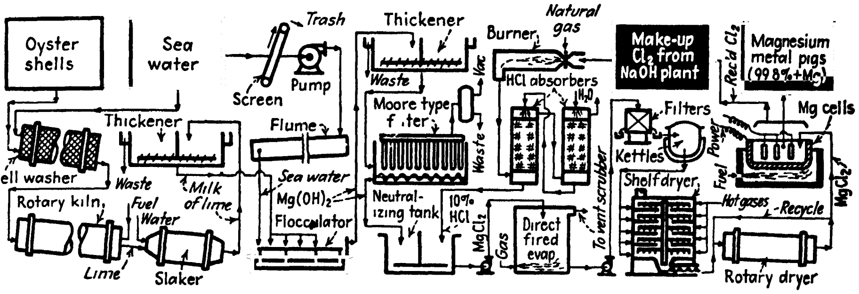

FIG. 3.—Magnesium metal from sea water—Dow process.

Basic Magnesium, Inc., produces their magnesium chloride from magnesite (magnesium carbonate), which is roasted to form magnesium oxide. The magnesium oxide is mixed with coal, peat moss, and a binder and chlorinated at around 850°C. in an electrically heated furnace in an atmosphere of chlorine. Molten anhydrous magnesium chloride is produced[2] according to the reaction:

$$MgO + C + Cl_2 \xrightarrow{850°C.} MgCl_2(l) + CO$$

Electrolysis of the magnesium chloride is carried out in a ceramic-lined, rectangular steel cell. There are six steel cathodes. The three anodes consist of graphite bars suspended vertically in the bath and shielded to collect the chlorine. Sodium chloride is added to the magnesium chloride to lower the melting point of the bath and also to increase the conductivity. The cells are heated by gas-fired furnaces to keep the baths molten. The usual operating temperatures are 670 to 730°C. This temperature is also sufficient to melt the magnesium formed. (Melting point of Mg is 651°C.) The voltage is about 6 volts and the current density is 16 to 35 amp. per sq. in. The molten magnesium rises to the surface of the bath as it is liberated where it is protected from oxidation by a thin coating of the electrolyte. It requires 5 lb. of magnesium chloride and 8 kw.-hr. in the cells to produce 1 lb. of metallic magnesium. The purity of the metal produced is greater than 99.9 per cent.[1]

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[1] KILLEFFER, *op. cit.*, flow charts and pictures; ANON., Magnesium from Sea Water, *Chem. & Met. Eng.*, **48**, No. 11, 130 (1941), pictured flow sheet.

[2] MCINDOE, Notes on the Pacific Coast Production of Metallic Magnesium, *Chem. Industries*, **49**, No. 1, 308 (1941); RAMSEY, Magnesium, Production at the World's Largest Plant, *Chem. & Met. Eng.*, **50**, No. 10, 98 (1943) flow chart and description.

Carbon Reduction.[2]—This process involves the electrothermal reduction of magnesium oxide with carbon. This is the most common method of reducing most metals from their ores. However, the reduction of magnesium requires much higher temperatures than would be expected from the boiling point of magnesium (1110°C.). Thermodynamic calculations indicate that the equilibrium temperature at atmospheric pressure and using stoichiometric quantities, as shown by the equation, is approximately 1800°C. These data indicate that at temperatures lower than 1800°C. the carbon monoxide acts as an oxidizing agent and thus reverses the reaction.[3]

$$MgO + C \rightleftharpoons Mg + CO$$

This difficulty has been overcome by running the reaction above 2000°C. and by "shock-cooling" the magnesium vapor by dilution with an inert gas such as natural gas or hydrogen.

Magnesia, obtained from dead-burned magnesite or by dehydration of magnesium hydroxide, is mixed with petroleum coke and formed into briquettes using pitch as a binder. The briquettes are fed continuously into a totally enclosed carbon-brick lined, three-phase electric arc furnace. As carbon is a good electrical conductor, a rapid flow of cold hydrogen is maintained between the electrodes and the furnace lining to provide insulation and to prevent reaction of carbon. The furnace is operated at 2100°C., and the vaporized products are drawn off through a special valve.

The vaporized magnesium mixed with carbon monoxide is condensed by cooling it with an inert gas. The original process utilized hydrogen for this purpose. The only plant in the United States utilizing this process is that of the Permanente Metals Corporation in California; it uses natural gas. Twenty-five volumes of gas are needed for each volume of the furnace vapors to lower the temperature of these vapors to 150 to 200°C. The magnesium obtained is in the form of a fine dust and is collected by electrostatic precipitators. About 75 per cent of the natural gas is recirculated; the rest is used for fuel.

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[1] Mantell, "Industrial Electrochemistry," 2d ed., McGraw-Hill Book Company, Inc., New York, 1940; Perry, *op. cit.*, pp. 2798–2799, gives data and cross section of cell.

[2] This is frequently called the *Hansgirg* process.

[3] Doerner, Holbrook, Dilling and Harris, Magnesium by Electrothermic Reduction, *U.S. Bur. Mines, Repts. Investigations* 3635, May, 1942; Doerner, Present Outlook for a Magnesium Industry in the Northwest, *op. cit.*

The magnesium dust contains about 60 to 65 per cent magnesium, contaminated with magnesium oxide and carbon. This dust is compressed and sublimed in electrical retorts at 750°C. under a high vacuum. Each retort furnishes 1 ton of magnesium every 72 hr.[1] and produces material of better than 99 per cent purity.

Ferrosilicon Reduction.—This process was developed by L. M. Pidgeon of the Canadian Research Council and Glen D. Bagley of the Union Carbide & Carbon Research Laboratories, Inc., and is being exploited commercially by Union Carbide and Carbon Corp., Ford Motor Co., the Dominion Magnesium Co. in Canada, and a number of other companies. The essential reaction can be represented by the equation:

$$2MgO + 2CaO + Si \rightarrow 2Mg + 2CaO{\cdot}SiO_2$$

The silicon is obtained from ferrosilicon. The process consists of mixing ground dead-burned dolomite with ground ferrosilicon and pelleting. The pellets are charged into the furnace, the high vacuum and the heat (1150°C.) applied. The calcium oxide present in the burnt dolomite forms infusible dicalcium silicate that is easily removed from the retort at the end of the run. The chrome-alloy retort is equipped with a condenser tube with a removable lining. The reaction is run at very high vacuum (a fraction of a millimeter), and the magnesium that is liberated is collected on the lining of the condenser. At the end of the run the furnace is partly cooled and the magnesium is removed from the condenser by the differential contraction of the magnesium and the steel. This magnesium does not require any additional purification.[2]

SODIUM AND POTASSIUM

Sodium and potassium are silvery white, very active metals. They react violently with water and thus are usually preserved by storage under kerosene or in containers free from water. The production of sodium is far greater than that of potassium. The uses of metallic sodium may be divided as follows: 50 per cent for the production of tetraethyl lead, 40 per cent for the production of sodium cyanide, and

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[1] Kirkpatrick, Magnesium by the Hansgirg Process, *Chem. & Met. Eng.*, **48**, No. 9, 91 (1941).

[2] Bagley, Calcium and Magnesium, Development of the Electrometallurgical Co.'s Process for Their Production, *Chem. Eng. News*, **22**, 221 (1944); Killeffer, Magnesium from Dolomite by Ferrosilicon Reduction, *Chem. Eng. News*, **20**, 369 (1942); Breyer, Pidgeon Ferrosilicon Process for Magnesium, *Chem. & Met. Eng.*, **49**, No. 4, 87 (1942); Anon., Magnesium Made in Canada, *Chem. & Met. Eng.*, **50**, No. 9, 101 (1943).

10 per cent for miscellaneous uses such as a chemical reagent in the manufacture of indigo. Potassium is used only as a specialized chemical reagent. Very few uses are found for potassium for which sodium cannot be substituted. The present cost of sodium is about 15 cents per lb., while that of potassium is about 15 cents per oz.

Manufacture.—The most important method of preparation of these two metals is by the electrolysis of fused sodium or potassium chloride.

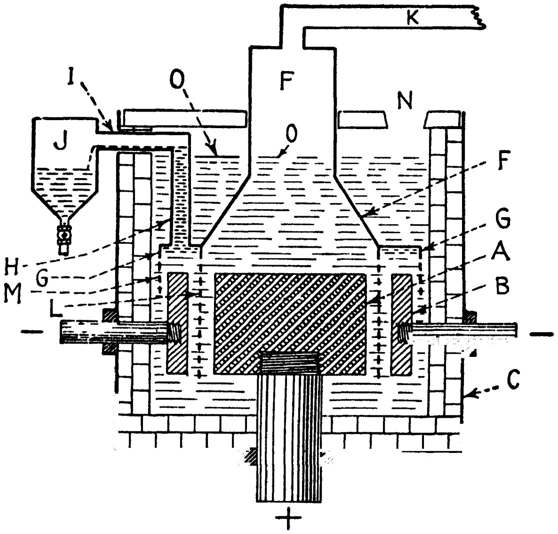

FIG. 4.—Downs's sodium cell. *A* is the graphite anode, *B* is the iron cathode, *F* is the dome for collecting the chlorine, and *K* the pipe for conducting this chlorine away. *G* is the annular sodium collector with *H* and *I* as pipes to conduct this sodium to the vessel *J*. *L* and *M* are metal screens supported by *F* and serving to separate the cell products. *C* is the shell of the cell made of steel but lined with refractory bricks. *N* is the charge port for salt and *O* is the bath level.

Originally, most of the metallic sodium was produced by the electrolysis of fused caustic soda, but the salt process has practically supplanted this older process. The newer procedure has the advantages that it uses a natural raw material, NaCl, instead of a manufactured product, NaOH (see Chap. XV), and also that it produces a valuable by-product, chlorine.

The reaction involved in this process is as follows:

$$2NaCl \rightarrow 2Na + Cl_2$$

The cell for this electrolysis consists of a closed, rectangular refractory-lined steel box (see Fig. 4). The anode is made of carbon and the cathode of iron.[1] The anode and cathode are arranged in separate compartments to facilitate the recovery of the sodium and the chlorine. Sodium chloride has a high melting point (804°C.), but other salts are added to lower this melting point so that the cell is operated at 600°C. These addition salts belong to the group of alkali and alkaline earth fluorides and chlorides such as calcium chloride. This lower temperature increases the life of the refractory lining of the cell, makes it easier to collect the chlorine, and prevents the sodium from forming a difficultly recoverable fog.

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[1] DOWNS, Electrolytic Process and Cell, U.S. Pat., 1501756, July 15, 1924. Downs received the Schoellkopf medal in 1934 for the development of this cell.

HYDROGEN PEROXIDE

Hydrogen peroxide,[1] H_2O_2, may be prepared by two electrolytic methods and also by an ordinary chemical process. It is sold in water solution, the common strengths being 3 grams and 30 to 40 grams per 100 cc. The two strong solutions are surprisingly stable. Many new uses for this chemical are being currently developed. At present it is widely used as a bleach, particularly for silk, wool, feathers, fur, and other *animal* fibers, as a mild antiseptic, in the manufacture of metallic peroxides, and in the making of "per" salts. Its unique property is that water is the only by-product of its oxidizing action. The rate of oxidation is much influenced by temperature, concentration, and the pH of the medium; buffers are added to control the pH as the reaction proceeds (silicates, phosphates, or carbonates). Its sale has so increased in recent years that tank-car shipments of the strong solutions are not uncommon.

Manufacture.—The main processes for the manufacture of hydrogen peroxide are the steam hydrolysis of persulfuric acid, wherein the vaporized hydrogen peroxide is fractionated and condensed, the treatment of ammonium persulfate with sulfuric acid, and the reaction of barium peroxide with phosphoric and sulfuric acids. Actually, electrolytic action enters only into the production of the raw materials. Persulfuric acid is obtained by the electrolytic oxidation of sulfuric acid as shown in the following reactions:

Cell reaction:

$$2H_2SO_4 \rightarrow H_2S_2O_8 + H_2$$

Steam distillation:

$$\underline{H_2S_2O_8 + 2H_2O \rightarrow 2H_2SO_4 + H_2O_2}$$

Over-all balance:

$$2H_2O \rightarrow H_2O_2 + H_2$$

Barium peroxide is not prepared electrolytically but by the passing of dry air or oxygen over barium oxide at 600°C. This process may be symbolized as follows:

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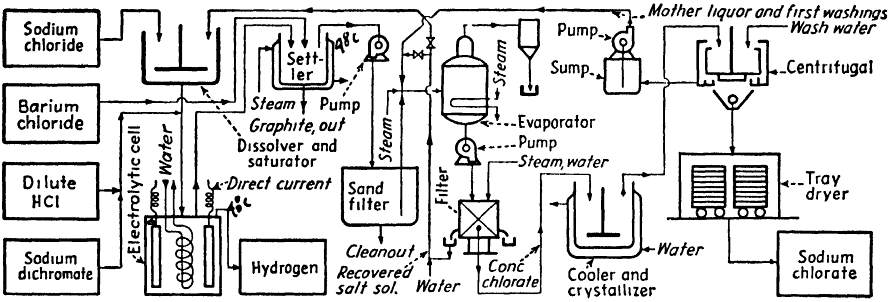
[1] REICHERT, Hydrogen Peroxide, *Chem. Eng. News*, **21**, 480 (1943).

$$
\begin{array}{c}
BaCO_3 + C \rightarrow BaO + 2CO \\
BaO + \tfrac{1}{2}O_2 \rightarrow BaO_2 \\
\underline{BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2} \\
BaCO_3 + C + \tfrac{1}{2}O_2 + H_2SO_4 \rightarrow BaSO_4 + 2CO + H_2O_2
\end{array}
$$

SODIUM CHLORATE AND PERCHLORATE

Sodium chlorate is manufactured in large quantities (about 20,000 tons annually) as a weed killer. It is also used in textile printing and dyeing. It cannot be employed in explosives because of its hygroscopicity, although potassium chlorate is satisfactory in explosives, matches, and fireworks. Sodium perchlorate does not have many commercial applications because of its extreme solubility in water but is used to prepare potassium and ammonium perchlorates which are consumed in explosives.

Manufacture.—Sodium chlorate[1] is produced by the electrolysis of saturated acidulated brine mixed with sodium bichromate (about 2 grams per liter) to reduce the corrosive action. Figure 5 shows the essential steps in the production of this chemical. The brine solution is made from soft water or condensate from the evaporator and rock salt. Mud collects at the bottom of the dissolver and storage tank. The rectangular steel cell is filled with either the brine solution or recovered salt solution made from recovered salt containing chlorate, dissolved in condensate from the evaporator. Sodium bichromate and dilute hydrochloric acid are added to the brine, and the temperature of the cell is maintained at 40°C. by cooling water. The purpose of the sodium



Salt (sodium chloride)	1,130 lb	Electric power (D C)	5 100 kw-hr.	To produce 1 ton of sodium chlorate
Hydrochloric acid	27 lb	Steam	11,000 lb	
Sodium dichromate	1 lb	Motor requirements	85 hp-hr	
Barium chloride	13 lb	Water (at 77 deg F)	60,000 gal	
Graphite consumed	17 lb	Labor	8 man hr	

FIG. 5.—Flow sheet for manufacture of sodium chlorate.

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[1] GROGGINS, *et al.*, Sodium Chlorate Production, *Chem. & Met. Eng.*, **44,** 302 (1937); **45,** 692 (1938); FURNAS, "Rogers' Manual of Industrial Chemistry," 6th ed., p. 458.

bichromate is to inhibit corrosion of the cell by the hypochlorous acid liberated by the hydrochloric acid present. The products of the electrolysis *are actually sodium hydroxide at the cathode and chlorine at the* anode but, as there is *no diaphragm* in the cell, mixing occurs and sodium hypochlorite is formed which is then oxidized to chlorate. The over-all reaction is

$$NaCl(aq) + 3H_2O(l) \rightarrow NaClO_3(aq) + 3H_2(g); \qquad \Delta H = +223{,}900 \text{ cal.}$$

The finished cell liquor is pumped to tanks where it is heated with live steam to 90°C. to destroy any hypochlorite present. The liquor is analyzed to determine the chromate content, and the required amount of barium chloride is introduced to precipitate almost all of the chromate present. The graphite mud from the electrodes and the barium chromate settle to the bottom of the tank, and the clear liquor is pumped through a sand filter to evaporator storage tanks. The liquor in the storage tank is neutralized with soda ash and is evaporated in a double-effect evaporator until it contains approximately 700 grams per liter of sodium chlorate. After evaporation, the liquor is allowed to settle to remove the sodium chloride which constitutes the *recovered* salt and chlorate, to be used over again. The settled liquid is filtered and cooled. This cooling requires 3 to 5 days, and the crystals of sodium chlorate form on the walls and bottom of the coolers. The crystals are spun in a centrifugal and dried in tray driers.

OTHER PRODUCTS

Elsewhere in this book a few electrolytic processes are presented as in the special chapter (XV) pertaining to caustic soda and chlorine. Electrolytic hydrogen and oxygen are included with the other procedures for hydrogen in Chap. VIII on Industrial Gases.

ORGANIC COMPOUNDS

Electroorganic chemical preparations are not of great commercial importance at the present time although the literature contains much information on organic reactions that can be carried out by the aid of electricity.[1] One of the few industrially important organic electrolytic reactions is the production of mannitol and sorbitol from glucose.

Figure 6 is a flow sheet for the manufacture of mannitol and sorbitol. This reaction involves the reduction of the aldehyde group in glucose to an alcohol group and also may be made to modify the stereochemical arrangement of the atoms in the glucose.[1] Thus, the electrolytic reduction of *d*-glucose yields sorbitol, which has the same stereoisomeric structure as glucose, and mannitol, which has the configuration of mannose.

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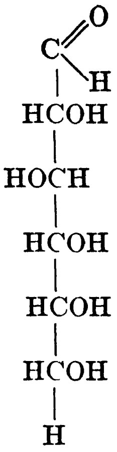
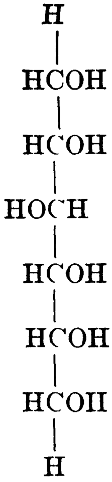
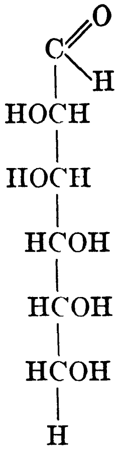
[1] For an extensive list of electrochemical preparations see SWANN, Electro-organic Chemical Preparations, I and II, *Trans. Electrochem. Soc.*, **69**, 287 (1936); **77**, 459 (1940).



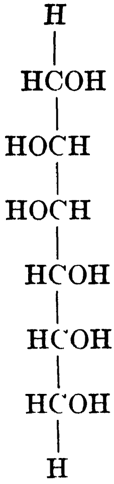
d-Glucose



d-Sorbitol



d-Mannose



d-Mannitol

The hydrogen for the reduction is supplied by the electrolysis of the water of the electrolyte solution. The sodium hydroxide and sodium sulfate are added to give electrical conductivity to the glucose solution. Figure 6 is self-explanatory in most of the details of this process. The two products, mannitol and sorbitol, are separated by taking advantage of the fact that mannitol may be crystallized from a diluted alcohol solution, while sorbitol will not deposit as crystals.

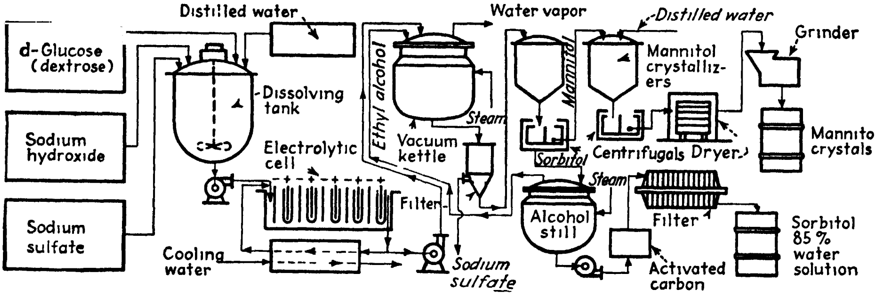


FIG. 6.—Mannitol and sorbitol from glucose.

It is interesting to note that the anodes of the cell should be surrounded by an unglazed porcelain diaphragm to prevent the sulfuric acid, formed during the electrolysis from the sodium sulfate, from coming in contact with the glucose solution. The equipment should also be rubber- or glass-lined to counteract the corrosive action of the dilute acid.

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[1] TAYLOR, Sorbitol from Glucose by Electrolytic Reduction, *Chem. & Met. Eng.*, **44**, 588 (1937).

PRIMARY AND SECONDARY CELLS

Chemical reactions can be utilized to convert chemical energy into electrical energy, the converse of the procedures presented in the earlier parts of this chapter. The chemical reaction can be caused to take place in a unit specially designed for the purpose of obtaining the electrical energy. These units are commonly called *cells* or *batteries.*[1] Primary cells produce electricity by means of a chemical reaction that is not easily reversible, and thus the chemicals must be replaced after the reaction has taken place. Secondary cells depend upon chemical reactions that are reversible by electrical energy and thus do not require replacement of the chemical components. Obviously then the cost of electrical energy from primary batteries is very high, especially if they are used for the production of large quantities of energy.

The commonest primary cell today is the *dry cell.* This consists of a zinc container which serves as one electrode and a carbon rod which is the other electrode. The electrolyte is a water solution of ammonium chloride and zinc chloride adsorbed in flour or starch and manganese dioxide. The manganese dioxide is added as a depolarizer. Graphite is usually introduced into this mixture to increase the conductivity. The whole cell is insulated by a cardboard container.

The most important secondary cell is the *lead storage battery.* The reactions that take place on discharge are

At positive plate:

$$\begin{array}{c} PbO_2(s) + 4H^+(aq) + 2e \rightarrow Pb^{++}(aq) + 2H_2O(l) \\ \underline{Pb^{++}(aq) + SO_4^{--}(aq) \rightarrow PbSO_4(s)} \\ PbO_2(s) + 4H^+(aq) + SO_4^{--}(aq) + 2e \rightarrow PbSO_4(s) + 2H_2O(l) \end{array}$$

At negative plate:

$$\begin{array}{c} Pb(s) \rightarrow Pb^{++}(aq) + 2e \\ \underline{Pb^{++}(aq) + SO_4^{--}(aq) \rightarrow PbSO_4(s)} \\ Pb(s) + SO_4^{--}(aq) \rightarrow PbSO_4(s) + 2e \end{array}$$

The over-all reaction would then be:

$$Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{--}(aq) \rightarrow 2PbSO_4 + 2H_2O$$

Electrical energy is generated when these reactions take place. To restore the activity or recharge the battery, electrical energy is applied to it and the reactions are reversed. On discharge, the *negative* plate acts as an anode and on charge as a cathode. On discharge, the *positive plate acts as a cathode and on charge as an anode. The battery consists of lead plates in the form of a grid filled, when charged, with lead peroxide on the positive plate and sponge lead on the negative plate.* The plates are insulated from each other by means of separators which formerly were made of cedar but at present are made of glass. The battery is filled with dilute sulfuric acid. The ordinary battery consists of 13 or 15 plates per cell and has 3 cells in series. It will deliver 2 volts per cell or 6 volts for the complete battery.

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[1] PERRY, *op. cit.*, pp. 2754–2763, gives diagrams and descriptions of various cells.

The only other widely used secondary cell is the *Edison battery.*[1] The positive plate consists of nickel peroxide and flaked metallic nickel; the negative plate is finely divided iron. The electrolyte consists of a mixture of potassium hydroxide and lithium hydroxide.

Problems

1. If finely pulverized iron costs 10 cents per pound, 30 per cent muriatic acid 1.05 cents per pound, and electricity 1 cent per kilowatt-hour, what is the comparative price for a pound atom of active reducing hydrogen produced (1) from iron and hydrochloric acid and (2) by the passage of the electric current if 2 volts are required to release the hydrogen?

2. "10 volume" hydrogen peroxide will liberate upon acidification at 60°F. and under normal barometric pressure oxygen whose volume is ten times the volume of the original solution. What is the percentage of hydrogen peroxide in the original water solution?

3. A bauxite sample runs 61 per cent Al_2O_3 and 8 per cent SiO_2. This material is roasted, dissolved in caustic soda to form a solution from which the iron present is precipitated by dilution and oxidation, then removed by filtration. By suitable treatment hydrated Al_2O_3 is precipitated in a very pure form with a recovery of 80 per cent of the original Al_2O_3. The SiO_2 remains behind as Na_2SiO_3. The precipitated hydrated Al_2O_3 is dehydrated and forms the charge to an aluminum furnace. If caustic soda is purchased as a solution in water containing NaOH equivalent to 38.8 per cent Na_2O at a cost of 1.3 cents per pound of solution, what will be the cost of the caustic soda used in producing 100 lb. of pure Al_2O_3 assuming that there is used 10 per cent more than the theoretical amount of NaOH required to react with the silica and Al_2O_3 present in the original bauxite? Note that most of this caustic soda is concentrated and reused.

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[1] PERRY, *op. cit.*, p. 2762.

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CHAPTER XVII

ELECTROTHERMAL INDUSTRIES

Many chemical products, made at high temperatures, demand the use of an electric furnace. Electric furnaces are capable of producing temperatures as high as 4100°C. This may be contrasted with the highest commercial combustion-furnace temperatures of somewhat under 1500°C. The effects of high temperature are twofold: the *speed* of the reaction is *increased* and *new conditions* of *equilibrium* are established. These new equilibrium conditions have resulted in the production of compounds unknown before the electric furnace. Silicon and calcium carbides are examples of new products thus formed. The electric furnace affords more exact control and more concentration of heat with less thermal losses than is possible with other types of furnace. This favorable situation is caused by lack of flue gases and by the high temperature gradient between the source of heat and the heated mass. The electric furnace is much cleaner and more convenient to operate than the combustion furnace. It is operated by alternating current of large amperage usually with moderate voltage, while the electrolytic industries require direct current.

The three chief types of electric furnaces are arc, induction, and resistance. The heat in the arc furnace is produced by an electric arc between two or more electrodes, which are usually graphite or carbon and may or may not be consumed in the operation. The furnace itself is generally a horizontal cylindrical shell lined with a refractory material. Its use is not limited to those industries for which it is a necessity. There are 12 companies with rolling-mill operations on common quality steels where electric arc furnaces are the sole source of their ingots.[1]

The induction furnace may be applied only for conducting substances such as metals where the electrical energy is converted into heat by the induced currents set up in the charge. The furnace can be considered as a transformer with the secondary consisting of the metallic charge while the primary consists of heavy copper coils connected to the power source. High-frequency furnaces with 6,000 cycles per sec. require much weaker field strength than low-frequency furnaces of 60 cycles per sec. The charge should be placed around an iron core in the low-*frequency furnace*, but this core is unnecessary for high-frequency *furnaces*.

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[1] Moore, Present Status of the Electric Arc Furnace in Industry, *Trans. Electrochem. Soc.*, **77**, 53 (1940).

When the charged material furnishes the electrical resistance required for the necessary heat, the furnace is a *direct-heated* resistance one; when high-resistance material is added to the charge for the purpose of creating heat, the furnace is *indirect-heated*.[1] In the electrochemical industry, the arc and the resistance furnaces are used mostly.

ARTIFICIAL ABRASIVES

History.—Previous to 1891 all the abrasives used were natural products such as diamonds, corundum, emery, garnet, quartz, kieselguhr, and rouge. In that year E. G. Acheson produced the first man-made abrasive in a homemade electric arc furnace while attempting to harden clay. Acheson found these new hard purple crystals to be silicon carbide. Discovering that these crystals were hard enough to cut glass, he sold them, under the trade-mark Carborundum, to gem polishers for $880 per lb.[2] Another make of silicon carbide is sold under the trade-mark Crystolon. Fused aluminum oxide, the most extensively used abrasive, is manufactured in the electric thermal furnace. Boron carbide, the hardest substance yet made synthetically, is also an electrothermal product.

Uses and Economics.—The discovery and production of artificial abrasives were the springboards for the evolution of modern grinding tools which are of paramount importance in the modern precise fabrication of multitudinous metal parts for automobiles, airplanes, rifles, cannon, and other manufactured items of present-day industrial endeavor. To reduce wear, harder and harder alloys are being developed by the metallurgist, many of which can be finally shaped economically only by these hard artificial abrasives. Silicon carbide is also used as a refractory material, in the form of both brick and refractory coating. In 1941 the United States and Canada produced 44,962 short tons of silicon carbide and 147,759 short tons of fused aluminum oxide. Of these quantities 32 per cent of silicon carbide and 3 per cent of aluminum oxide were used for nonabrasive purposes,[3] principally as refractories.

Silicon Carbide.—The raw materials for the production of silicon carbide[4] are sand and carbon. The carbon is obtained from anthracite, coke, tar, or petroleum coke. The sand contains 98 to 99.5 per cent silica. The equations usually given for the reactions involved are

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[1] Stansel, "Industrial Electric Heating," pp. 85–89, John Wiley & Sons, Inc., New York, 1933.

[2] Cooper, Modern Abrasives, *J. Chem. Education*, **19**, 122 (1942).

[3] Metcalf, Abrasive Materials, chapter from "Minerals Yearbook," 1941, U.S. Bureau of Mines, 1942.

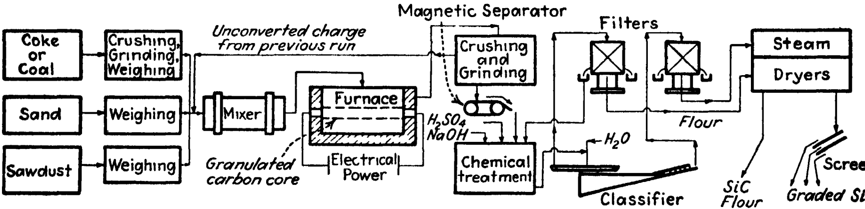
[4] Ruff, Formation and Dissociation of Silicon Carbide, *Trans. Electrochem. Soc.*, **68**, 87 (1935); Tone, High Temperature Products of Silicon, *Ind. Eng. Chem.*, **23**, 1312 (1931).

$$SiO_2 + 2C \text{ (amorph.)} \rightarrow Si + 2CO; \qquad \Delta H = +144{,}800 \text{ cal.}$$
$$Si + C \text{ (amorph.)} \rightarrow SiC; \qquad \Delta H = -30{,}500 \text{ cal.}$$

The total reaction, obtained by combining these equations, is

$$SiO_2 + 3C \text{ (amorph.)} \rightarrow SiC + 2CO; \qquad \Delta H = +114{,}300 \text{ cal.}$$

Figure 1 is a flow sheet for the production of silicon carbide. Sand and carbon are mixed in the approximate mole ratio of 1:3 and charged into the furnace. Sawdust is mixed with the charge to give off gas during the heating and thus increase the porosity of the carbide. The furnace is of the resistance type, and the charge is built up in the furnace around a heating core of granular carbon. This core is in the center of the 30- to 40-ft. furnace and connects the electrodes. The walls of the furnace are loose firebrick supported by iron castings and are taken away at the end of a charge to facilitate product removal. Excessive heat loss does not occur because the outside unreacted charge serves as an insulator. The initial current between the electrodes is 6,000 amp. at 230 volts and the final is 20,000 amp. at 75 volts.[1] This change in voltage is due to the decrease in the resistance of the charge as the reaction progresses. The temperature at the core is 2200°C. The temperature should not get too high or the silicon carbide will decompose with volatilization of the silicon and formation of graphite. Indeed artificial graphite was so discovered. The energy efficiency is about 50 per cent with a chemical conversion of from 70 to 80 per cent.



Sand	2.10 ton	Per ton finished silicon carbide (Including unconverted charge)
Coke	1.40 ton	
Sawdust (if used)	0.50 ton	
Electricity	8.000-9,000 kw-hr.	

Fig. 1.—Flow sheet for silicon carbide.

The time of the reaction is about 60 hr.: 36 hr. of heating and 24 hr. of cooling. After cooling, the silicon carbide crystals are removed with a yield of about 6 to 8 tons per furnace. The larger pieces of crystals are broken, washed, and cleaned by chemical treatment with sulfuric acid and caustic soda. The crystals are classified and screened, the finished

[1] Perry, *op. cit.*, p. 2813.

product ranging from 6 mesh to fine powder. The outer unreacted part of the charge is combined with the next charge for the furnace.

A part of the core used in the furnace can be made of coke suitable for graphite manufacture. After the run is completed, the graphite can be separated from the silicon carbide and converted to desired shapes.[1]

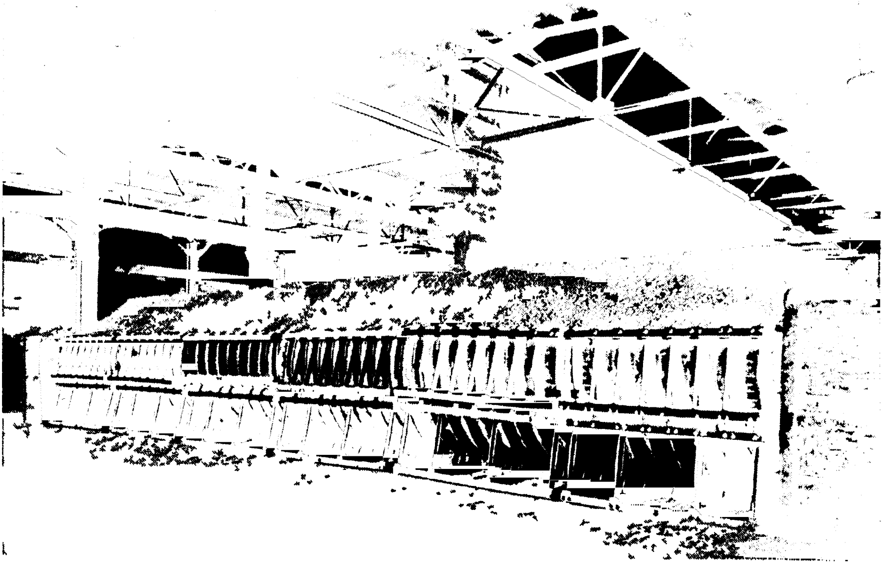


FIG. 2.—Electric-resistance furnace in which Carborundum brand silicon carbide is produced. (*Courtesy of The Carborundum Company*)

Fused Aluminum Oxide.—The raw material for fused aluminum oxide abrasives such as those sold under the trade-marks Alundum and Aloxite may be an impure bauxite, often called *red bauxite.* The impurities, mainly iron and silicon oxides, impart toughness to the finished abrasive. However, some pure alumina is also fused for particular demands as where the grinding wheel temperature must be kept low. In any case the aluminous material should be calcined before charging into the furnace.

The vertical arc resistance furnace consists of a crucible carbon base and conical steel sides built on a car. The electrodes are lowered into the furnace and arcs are produced between the electrodes and also between the electrodes and the base of the furnace. The charge to the furnace is calcined red bauxite, coke (3 per cent), and scrap iron (2 per cent). The charge is added as fast as it fuses between the arcs, and this molten alumina carries the current. As the level of fused alumina rises, the electrodes are raised and more bauxite is added until finally the furnace is full. Water is allowed to flow over the outside surface of the furnace so that the alumina around the walls solidifies and thus furnishes a refractory lining for the furnace. When the furnace is filled with molten alumina,[1] the current is shut off and the entire mass cooled under controlled conditions to obtain the texture desired. Although this product has the hardness 9 in the Moh scale for corundum, it is blebbular in structure and not uniform, and therefore bearings cannot be made from it. The cooled ingots are broken up by roll crushers, washed with chemical solutions, and sieved. The product is fabricated into abrasive wheels, papers, and powders, or into refractory shapes. For the hard bearings necessary for watches and modern instruments, *artificial corundum* or white sapphire is made by fusing *pure* alumina in a hydrogen-air upside-down flame by the Verneuil process. The crystal boules are cut and polished as desired. Many gems are also made by this same process.

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[1] VARZANOV and NEGOVSKII, Production of Graphite in Silicon Carbide Furnace, Russian Pat., 52908, Mar. 31, 1938.

Boron Carbide.[2]—This is the hardest abrasive ever made artificially, though far from the hardness of the diamond. It first made its appearance in 1934 under the name *Norbide.* The reaction for its production is as follows:

$$2B_2O_3 + 7C \rightarrow B_4C + 6CO$$

The boric oxide is caused to react with coke in a carbon resistance furnace at 2600°C. The product is about 99 per cent B_4C. It finds specialized use in such molded shapes as nozzles for sandblasting. Other such products as tungsten carbide are also manufactured.

CALCIUM CARBIDE

History.—The first production of calcium carbide was an accident. In 1895, Thomas L. Wilson was attempting to prepare metallic calcium from lime and tar in an electric furnace at Spray, N.C. The product obtained, obviously not calcium, was thrown into a near-by stream and Wilson was amazed to note that it liberated great quantities of combustible gas. The first factory for the production of calcium carbide was built at Spray in the same year.[3]

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[1] Perry, *op. cit.*, pp. 2813–2814, energy consumption and other technical data are given; Cooper, *op. cit.;* Riegel, "Industrial Chemistry," 4th ed., pp. 298–299, Reinhold Publishing Corporation, New York, 1942.

[2] Ridgway, Boron Carbide, *Trans. Electrochem. Soc.*, **66**, 117 (1934); U.S. Pat., 1897214; Manufactured abrasives—Old and New, *Chem. Eng. News*, **21**, 858 (1943).

[3] Pond, "Calcium Carbide and Acetylene," Pennsylvania State College, State College, Pa., 1909.

Uses and Economics.—Calcium carbide is consumed by two principal procedures: to manufacture cyanamide by combining it with nitrogen and to prepare acetylene by reacting it with water. The cyanamide is made by heating calcium carbide in an atmosphere of nitrogen (see Chap. XX). A substantial proportion of the total calcium carbide produced is converted to cyanamide.

Acetylene is a very important chemical used as a fuel for welding torches and as a raw material for a great variety of organic syntheses. Much of the acetic acid is produced by treating acetylene with water in the presence of mercurous sulfate followed by subsequent air oxidation

$$\underset{\text{Acetylene}}{CH{\equiv}CH + H_2O} \xrightarrow{Hg_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{O_2} \underset{\text{Acetic acid}}{CH_3CO_2H}$$

of the acetaldehyde first formed. Acetylene is also used to prepare the monomers from which vinyl polymers are formed (see Chap. XXXV). It likewise is the basis of the first successful synthetic rubber, Neoprene (Chap. XXXVI).

The annual United States production of calcium carbide is approximately 250,000 tons[1] in peace years.

Manufacture.—Calcium carbide is prepared from quicklime and carbon at approximately 2000°C. The source of carbon is usually coke, anthracite, or charcoal. Coke is most widely used. It should be

$$CaO + 3C\ (\textit{amorph.}) \rightarrow CaC_2 + CO; \qquad \Delta H = +103{,}000 \text{ cal.}$$

compact and have a low ash content, a low ignition point, and high electrical resistivity so that the bulk of the furnace charge is highly resistant to the flow of energy. Thus the energy is concentrated, resulting in more rapid and complete reaction. Phosphorus should be absent as it forms a phosphide which is converted to poisonous phosphine, PH_3, when the carbide is made into acetylene. The quicklime is produced by burning limestone containing at least 97 per cent calcium carbonate. Impurities such as magnesia, silica, and iron hamper production and give a less pure carbide.

The arc-resistance furnace used may be either an ingot or tapping furnace. The ingot furnace is similar to that used to produce fused aluminum oxide. A carbon electrode is lowered into a carbon-lined steel box on a car and strikes an arc with the bottom. The charge is added from time to time, and the electrode is raised until the furnace is full. The filled car is disconnected, cooled, and the ingot removed.

The tapping furnace produces molten carbide and consists of a steel shell lined with a carbon which is about the only refractory that with-stands these alkaline extremely hot conditions. The charge on the outside of the hot reacting zone also resists the reaction product. The arc is produced by three electrodes connected to three-phase electrical current. The lime and coke are charged continuously, and the molten carbide at 1800°C. is tapped almost continuously. The capacity of a 30,000-hp. furnace is about 185 tons[1] per 24 hours. The energy consumption is 1.5 to 3 kw.-hr. per lb. of commercial product usually 85 per cent carbide (equivalent to 4.75 cu. ft. of acetylene per pound).

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[1] PERRY, *op. cit.*, p. 2812.

The solidified carbide from either type of furnace is broken into pieces and graded for size in an atmosphere of nitrogen to prevent the possibility of explosion from any acetylene that may have been formed.

MISCELLANEOUS ELECTROTHERMAL PRODUCTS

Carbon Disulfide.—Over 150,000,000 lb. of carbon disulfide are produced in the United States annually with a value of around $5,000,000. Although it is employed mostly for the manufacture of viscose rayon, it does have many smaller uses such as for making carbon tetrachloride, as a solvent, and as an insecticide.

Carbon disulfide is made by the reaction:

$$C + 2S \rightarrow CS_2$$

This is carried out[2] at a relatively low temperature in a shaft electric arc furnace where the sulfur melted by the arc comes into contact with the charcoal, forming the carbon disulfide which is then volatilized. This is an illustration of the applicability of the electric furnace to specialized conditions with excellent efficiency. The furnace is constructed with an inner tube containing the charcoal and up which the carbon disulfide passes. Around this is a concentric ring with the sulfur. The multiple electrodes are at the bottom where the reaction occurs.

Fused Silica.—This very useful material of construction for the chemical industries is heated to fabrication temperature in an electric furnace.

Artificial Graphite and Electrodes.—These are described in Chap. IX devoted to carbon, while *phosphorus* is presented in Chap. XVIII on Phosphorus Industries. See also Table 2 in Chap. XVI for a summary of the various products made by electrochemical processes.

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[1] PERRY, *op. cit.*, p. 2812; MANTELL, "Industrial Electrochemistry," 2d ed., McGraw-Hill Book Company, Inc., New York, 1940; LANDIS, pp. 485–488, in "Rogers' Manual of Industrial Chemistry," 6th ed., D. Van Nostrand Company, Inc., New York, 1942. See flow sheet of Fig. 1 of Chap. XX. A pictured flow sheet is given in *Chem. & Met. Eng.*, **47**, 253 (1940).

[2] TAYLOR, Carbon Disulfide, *Trans. Am. Electrochem. Soc.*, **1**, 115 (1902); **2**, 185 (1902). PERRY, *op. cit.*, p. 2815 (data given); ULLMANN, "Enzyklopaedie der technischen Chemie," 2d ed., vol. 9, pp. 263–277, Urban & Schwarzenberg, Berlin and Vienna, 1928–1932, diagrams of furnace and plant.

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(See also preceding chapter)

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CHAPTER XVIII

PHOSPHORUS INDUSTRIES

Owing chiefly to an aggressive and intelligent consumption promotion on the part of the various manufacturers as well as the Federal agencies, the use of artificial fertilizers, phosphoric acid, and phosphate salts and derivatives has increased greatly. However, before these products could be as widely consumed in their fast developing fields, newer, more efficient, and less expensive methods of production had to be developed. During the past 20 years, the various phosphate industries have made rapid strides in cutting the costs of production and have thus enabled phosphorus, phosphoric acid, and its salts to be employed in wider fields, and newer derivatives to be introduced. The phosphorus industry has proved itself to be one branch of the inorganic field that has not been overshadowed by the fast-moving organic chemical developments of recent years. Indeed, phosphorus-organic compounds are of increasing industrial importance each year.

CALCIUM PHOSPHATES

Historical.—The use of phosphatic materials as fertilizers was practiced unknowingly long before the isolation and discovery of phosphorus by the German alchemist, Brand, in 1669. As early as 200 B.C., the Carthaginians recommended and employed bird dung for increasing the yields from their fields. The Incas of Peru prized guano and bird dung on their islands so highly that it was made a capital offense to kill any of the birds. Then too, we are all familiar with the use of fish and bones by the American Indian in his crude agricultural methods. Bones and guano continued to be the chief sources of phosphorus and phosphoric acid until after the middle of the nineteenth century, but these supplies were and still are limited.

In 1842 a British patent was issued to John B. Lawes for the treatment of bone ash with sulfuric acid. This patent marked the beginning of the large acid phosphate industry which became the basis of our domestic fertilizer industry.

Soon afterward various grades of phosphate ores were discovered in England. These were first finely ground and applied directly to the soil. It was soon recognized, however, that treatment of these phosphate minerals with sulfuric acid increased the availability and efficiency of the phosphate for agricultural purposes. This process was so eagerly adopted that by 1862 the annual production of superphosphates in England had reached 200,000 tons. Table 1 shows the United States statistics for the industry.

TABLE 1.—STATISTICS FOR SUPERPHOSPHATE INDUSTRY IN THE UNITED STATES[a]

	1938	1939	1940	1941
Production:				
Bulk superphosphate, short tons.....	3,575,588	3,801,194	4,385,971	4,867,202
Wet base and mixed goods, short tons	156,730	152,500	136,204	136,631
Exports of superphosphate, long tons.	90,237	95,224	141,289	102,784[b]
Imports of superphosphate, long tons...	18,753	17,238	10,017	6,980[b]
Sales of phosphate rock by producers for superphosphate production, long tons.	2,074,779	2,192,779	2,564,844	2,825,456

[a] "Minerals Yearbook," 1941, p. 1385.

[b] Figures cover January to September, inclusive.

TABLE 2.—USE DISTRIBUTION OF PHOSPHATE ROCK IN THE UNITED STATES[a]

Consuming industries	1940, long tons	1941, long tons
Superphosphate..................................	2,564,844	2,825,456
Phosphates, phosphoric acid, phosphorus, ferrophosphorus..................................	532,980	644,948
Direct application to soil..................................	106,292	143,196
Fertilizer filler..................................	32,804	1,074,712
Stock and poultry feed..................................	1,311	
Undistributed..................................	6,747	
Exports..................................	757,722	
Total, long tons..................................	4,002,700	4,688,312
Total value..................................	$12,334,662	$15,587,738

[a] "Minerals Yearbook," 1941, p. 1374.

Raw Material.—Phosphate rock, when very finely pulverized, has an important but limited use (Table 2) as a fertilizer itself, owing chiefly to the relatively slow availability of the P_2O_5. Its chief consumption is as a raw material for the manufacture of phosphoric acid and superphosphate.

Although Florida and Tennessee are the main producing areas, phosphate rock of commercial grade and quantity is known to exist, though not in continuous beds, in the Western states all the way from central Utah to the Canadian boundary, and also into Canada. Utah, Idaho, Wyoming, and Montana contain the most extensive deposits.

Mansfield[1] has recently reported in detail on the phosphate deposits, indicating that the United States has reserves of over 13,500,000,000 metric tons or about 51 per cent of the world's total. Table 3 shows phosphate rock mined over a period of years.

TABLE 3.—PHOSPHATE ROCK MINED IN THE UNITED STATES[a]

Average value at mine per long ton	Year	Florida, long tons	Tennessee, long tons	Western States, long tons	United States, long tons
$3 54	1934	2,464,969	394,311	38,958	2,898,238
3.60	1935	2,598,337	493,501	67,490	3,159,328
3.40	1936	2,645,819	737,866	79,152	3,462,837
3.28	1937	3,179,588	942,158	139,670	4,261,416
3.46	1938	2,722,927	999,551	137,998	3,860,476
3.27	1939	2,791,360	1,057,570	139,040	3,987,970
3.08	1940	2,782,956	1,120,551	164,570	4,068,077
3.32	1941	3,417,900	1,301,067	201,876	4,920,843

[a] "Minerals Yearbook," 1941, p. 1372.

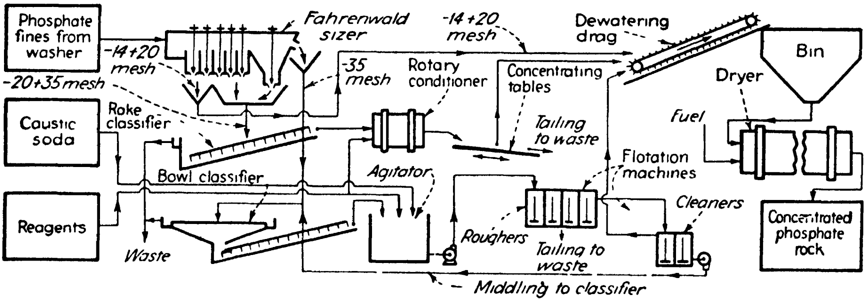

FIG. 1.—Beneficiation of fines under 14 mesh from Florida pebble phosphate rock. Reagents, labor, and power vary widely with conditions. (*Courtesy of Phosphate Recovery Corporation.*)

Unlike the large deposits of phosphate rock in Florida and Tennessee, the Western deposits resemble fissure veins. For example, the rock may exist as a vein from 3 to 5 ft. thick extending through a hill several hundred feet higher than the surrounding country. The rock lies between a wall of limestone on one side, and of shale or clay on the other. It contains approximately 75 per cent bone phosphate of lime[2] but, owing to admixture of the rock with wall material, it usually averages nearer 70 per cent b.p.l. and, owing to its rather soft structure, the rock has a moisture content of 4 to 6 per cent. This rock is generally mined by underground methods.

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[1] MANSFIELD, Phosphate Deposits of the World, *Ind. Eng. Chem.*, **34**, 9 (1942); *cf.* Chap. XXXIII, Phosphate Rock, by Martin and Wilding in "Industrial Minerals and Rocks," American Institute of Mining and Metallurgical Engineers, 1937; MANSFIELD, Phosphate Resources of Florida, *Bull.* 934, United States Geological Survey, Washington, 1943.

[2] This is usually abbreviated b.p.l. and actually means tricalcium phosphate, that being the chief inorganic constituent of bones.

The phosphate rock in the land pebble deposits of Florida and in the brown rock deposits of Tennessee should first be processed in order to bring its bone phosphate of lime content up to at least 66 or 68 per cent. This procedure is frequently spoken of as *beneficiation* and is illustrated by Fig. 1. Such upgrading operations are of far-reaching and increasing importance as the easily mined or better grade deposits of phosphate rock, or any other mineral, become exhausted. These operations not only produce a higher grade of product but enable larger amounts to be recovered, beneficiated, and used, even in the case of such a low-priced product as phosphate rock which sells in the price range of $2 to $4 per long ton.

In Tennessee the beneficiation procedure is applied to about 150,000 long tons of phosphate rock per year, raising its b.p.l. from 60 to 72 per cent, thus making more valuable an already good product. However, in the Florida pebble field this beneficiation of the fines accounts for more than half of the production or for approximately 1,500,000 long tons annually, starting with what was and would be an otherwise waste product analyzing only 20 to 45 per cent b.p.l. It is beneficiated up to 68 or more b.p.l. In this Florida pebble district, the recovery was initially only of the coarse phosphate rock while the fines, representing about an equal[1] tonnage of b.p.l., were wasted. Figure 1 illustrates[2] how these fines are recovered by sizing and froth flotation, thus doubling the yield per acre and making workable many of the deposits that produced too little of the coarse b.p.l. Naturally the flotation reagents vary with the specific deposit, but typical reagents are fatty acid from fish oil and fuel oil together with caustic soda for pH adjustment. When working on the low grade fines (14 mesh and under) coming from the washer screens of the Florida phosphate operations, experience has shown that these once wasted fines should be size-separated into three parts as follows, using a Fahrenwald sizer:

1. *Coarsest:* +20 mesh; sufficiently high grade to be dried and sold.
2. *Intermediate.* −20, +35 mesh; too coarse for flotation. This size is handled on a rake classifier and concentrating tables as shown in Fig. 1, or by other sizing equipment such as the belt machine developed by Coronet Phosphate Co., or the underwater screening device of Swift & Co.

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[1] MARTIN and WILDING, *op. cit.*, p. 566. Bibliography.

[2] Courtesy of Phosphate Recovery Corp. of Florida and New York (William Trotter).

3. *Fines:* −35 mesh; oiled and treated in flotation cells as shown in Fig. 1. At one time a rod mill was used in the original circuit but this has been abandoned because it produced too much phosphate slime which could not be held and recovered in the flotation.

Uses and Economics.—Table 2 shows the great importance of phosphate rock for the United States. Tricalcium phosphate in the form of bone is also used as a raw material for phosphate chemicals or after grinding as a direct phosphate fertilizer. From the table it can be seen that some phosphate rock is applied directly on the soil after being dried and very finely ground, but most of it before such use as a fertilizer is treated with sulfuric acid to form superphosphate. However, it has long been recognized that in the soil much of the citrate soluble superphosphate is changed to water-insoluble tricalcium phosphate.[1] This is not a change from one form of $Ca_3(PO_4)_2$ to a finer divided one as "domestic phosphate rocks are essentially fluorapatite admixed with various proportions of other compounds of calcium, fluorine, iron, aluminum, and silicon."[2]

The formula of fluorapatite may be expressed,

$$(CaF)Ca_4(PO_4)_3 \text{ or } CaF_2{\cdot}3Ca_3P_2O_8$$

This compound is extremely insoluble. The various means for making the P_2O_5 content more soluble, not necessarily in water but in the plant juices,[3] are the manufacture of the various superphosphates and the recent defluorination of this fluorapatite by the melting at about 1450°C. of phosphate rock as studied by Jacobs and coworkers of the U.S. Department of Agriculture and particularly by Curtis and his associates of the T.V.A.

The uses to which phosphate compounds are put in the fertilizer field are largely dependent upon the solubilities or the availability to the plants. These compounds may be classified:

1. *Water insoluble products:* rock phosphate or fluorapatite, $CaF{\cdot}Ca_4(PO_4)_3$. This can be solubilized by the sulfuric acid of the superphosphate process or by the *slow* dissolving action of plant juices.

2. *Citrate soluble products:* dicalcium phosphate, $CaHPO_4$, commonly called *precipitated phosphate* or *precipitated bone;* basic slag, the calcium and potassium

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[1] Or to insoluble iron, aluminum, or magnesium phosphates. *Cf.* BEAR and TOTH, Phosphate Fixation in Soil and Its Practical Control, *Ind. Eng. Chem.*, **34,** 49 (1942). Band placement of the phosphate fertilizer reduces the soil fixation.

[2] ELMORE, HUFFMAN, and WOLF, Defluorination of Phosphate Rock in the Molten State, *Ind. Eng. Chem.*, **34,** 40 (1942). *Cf.* EASTERWOOD, Recent Development in the Phosphate Field, *Ind. Eng. Chem.*, **34,** 13 (1942), excellent bibliography; HENDRICK, HILL, JACOB, and JEFFERSON, Structural Characteristics of Apatite-like Substances and Composition of Phosphate Rock and Bone as Determined from Microscopical and X-ray Diffraction Examinations, *Ind. Eng. Chem.*, **23,** 1413 (1931).

[3] As measured by "citrate solubility."

metaphosphates, the defluorinated phosphates (calcined phosphates and fused phosphate rock). Also part of the tricalcium phosphate of bone meal is citrate soluble. These products are soluble in ammonium citrate solution and are considered to be available for plant food.

3. *Water-soluble products:* monocalcium phosphate, $CaH_4(PO_4)_2$, is the principal member of this class and is the chief ingredient of superphosphate. Here also are monoammonium and diammonium phosphates and monopotassium phosphate and some organic phosphates.

Manufacture of Superphosphate.—Superphosphate is made either by (1) the den process or (2) the granulation process. The acidulation of phosphate rock to produce superphosphate[1] has been the most important method of making phosphate available for fertilizer purposes for nearly a century. The reactions have long been given as

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O \rightarrow \underset{\substack{\text{Monocalcium}\\ \text{phosphate}}}{CaH_4(PO_4)_2} + \underset{\text{Gypsum}}{2(CaSO_4{\cdot}2H_2O)}$$

$$CaF_2 + H_2SO_4 + 2H_2O \rightarrow CaSO_4{\cdot}2H_2O + 2HF$$

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O$$

In water,

$$3SiF_4 + 2H_2O \rightarrow SiO_2 + 2H_2SiF_6$$

The following is a more probable expression of the main reaction:

$$\underset{\substack{\text{Phosphate}\\ \text{rock}}}{2[(CaF)Ca_4(PO_4)_3]} + 7H_2SO_4 + 17H_2O \rightarrow \underset{\substack{\text{Monocalcium}\\ \text{phosphate}}}{3CaH_4(PO_4)_2H_2O} + 2HF + 7(CaSO_4{\cdot}2H_2O)$$

The hydrofluoric acid reacts as shown above, forming fluosilicic acid. An excess of sulfuric acid is consumed by such impurities in the phosphate rock as, $CaCO_3$, Fe_2O_3, Al_2O_3, and CaF_2. The product increases in weight over the 70 to 75 per cent b.p.l. phosphate rock used as much as 70 per cent, resulting in a superphosphate with 16 to 20 per cent available P_2O_5. It has been said that a sulfuric acid plant is almost a requirement to a superphosphate plant[2] in order successfully and economically to produce the superphosphates. Chamber acid is used which is sulfuric acid of 50° to 55°Bé. or 62 to 70 per cent H_2SO_4.[3]

1. *Den Process.*[4]—The first step is the reduction of the phosphate rock to a finely divided state with a tendency toward finer grinding. Good practice indicates passage through a 100-mesh screen. Modern

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[1] PACKARD, Superphosphate—Its History and Manufacture, *Ind. Chemist,* **13,** 50–53 (1937); JACOB, MARSHALL, REYNOLDS, and TREMEARNE, Composition and Properties of Superphosphate, *Ind. Eng. Chem.,* **34,** 722 (1942).

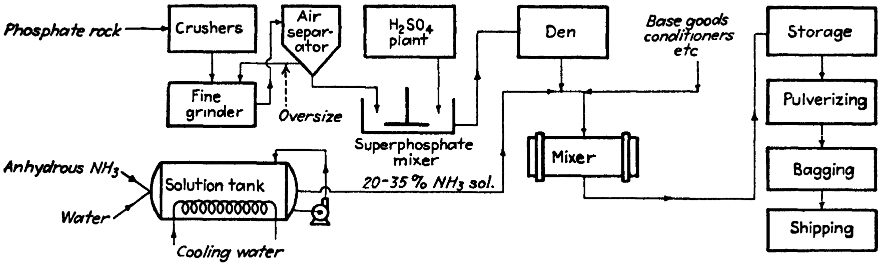
[2] *Cf.* MCBRIDE, Fertilizer Practice at Curtis Bay, *Chem. & Met. Eng.,* **47,** 4 (1940).

[3] PERRY, *op. cit.,* pp. 95, 429.

[4] MCBRIDE, *op. cit.* This plant uses a 72 per cent b.p.l. phosphate rock as a minimum and produces a 20 per cent available superphosphate.

grinding machinery and air separating equipment have helped make this degree of fineness possible with the following benefits: (1) the reaction with the acid and rock takes place faster, (2) more efficient use is made of the sulfuric acid with consequent less acid, (3) a higher grade of product in better condition is obtained. Figure 2 indicates the sequences of these steps.

The reaction between the sulfuric acid and the mineral rock in this method usually takes place in pan mixers. The mixer has a capacity of approximately 2 tons per charge, is of lead-covered cast iron, and may be approximately 8 ft. in diameter and 2½ ft. in depth. The pan itself is sometimes revolved on a vertical axis, while a set of blades is rotated in the opposite direction. The phosphate rock and a predetermined quantity of chamber sulfuric acid (50 to 55°Bé.) are usually added simultaneously to the mixer and agitated 2 to 3 min. The sirupy mixture is usually dumped directly into a "den" below the mixer. The den may be rectangular in shape, but it is frequently of a cylindrical or silo type and is constructed of concrete or brick, holding 100 or more tons. To ensure complete reaction, the material is left in the den for 6 to 24 hr. The temperature of the mass is usually above 100°C., and carbon dioxide, steam, and gaseous compounds of fluorine escape, leaving a fairly dry and porous product. The superphosphate is removed from the den by means of a clamshell shovel and overhead crane and is transferred to the storage pile where it is allowed to cure for 8 to 10 weeks. The superphosphate may be sold in this form directly, or it may be artificially further dried and disintegrated to a uniform size.[1] There should not be any free sulfuric acid left or the bags will be rotted.



Phosphate rock	1,000 lb.	Water	27-30 gal.	Per ton ammoniated superphosphate
Sulfuric acid (52deg. Be!)	900 lb.	Power and labor	Variable	
Ammonia (anhydrous)	70-80 lb.			

FIG. 2.—Flow sheet for superphosphate and its ammoniated derivative. The product from the den is also sold after aging, pulverizing, and bagging.

2. *Granulated Superphosphate.*—The granulation of superphosphate and superphosphate mixtures has been in the process of development

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[1] PERRY, *op. cit.*, p. 1939, particularly considers the special problems involved in pulverizing monocalcium phosphate.

since 1926. The newest or Davison[1] method is now operating to make 2,000 tons per day. It starts with the superphosphate as it comes from the den in the regular process. Up to this point the new and the old processes are similar. The moist and warm crude superphosphate is brought by crane from the den to a feed hopper for the granulating and conditioning system. A variable-speed screw feeder transfers classifier dust to a conveyer system where it is mixed in with this moist superphosphate. The second step is extremely important since the granulating properties of the superphosphate depend upon the moisture content. The superphosphate goes from the feeding device to a "conditioner" which is a rotating cylinder and where the material is subjected to water sprays to form balls or granules and to accelerate the chemical acidulation. An operator is stationed at the discharge end, to watch constantly the material discharged and to adjust the sprays as necessary.

The conditioned material is fed into the oil-fired rotary drier, which is about 8 ft. in diameter and 50 ft. long, and discharged into a pit at its lower end. The combustion gases are drawn from the lower end and forced by a draft fan through a cyclone dust collector. The material is aged for at least 10 days. Compare this with the 8 or 10 weeks of storage required by the old method.[2] The shorter period of cure is due to the accelerated acidulation of this process caused by improved mixing, proper moisture adjustment, and enhanced temperature. The granular product also is free flowing, handles and mixes better than the old powdery den product.

The first granulation process was the Oberphos process[3] bought out and superseded by the Davison process. The superphosphate reaction and granulation were performed in a closed, horizontal, rotary riveted or welded steel autoclave with a thin auotogenous lead lining and with 500 to 1000 cu. ft. capacity. It may or may not have been steam jacketed. The exothermic reaction raised the temperature to 300°F. and the pressure to 90 lb. per sq. in. The Oberphos process is still used in Canada and England.

Triple Superphosphate.—This material is a much more concentrated product than is the ordinary superphosphate and contains 48 to 50 per cent of available P_2O_5 or approximately three times the amount in the regular superphosphate. Instead of using sulfuric acid, this material is made by the action of phosphoric acid on the phosphate rock, and thus no calcium sulfate is formed.

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[1] McBride, *op. cit.;* Mackall and Shoeld, Granulating Phosphate Fertilizers, *Chem. & Met. Eng.*, **47**, 102 (1940).

[2] McBride, *op. cit.;* Mackall and Shoeld, *op. cit.;* parallel flow sheets are given as well as photographs. In *Chem. & Met. Eng.*, **50**, No. 4, 130 (1943) are given parallel pictured flow sheets for the den and granulated superphosphates.

[3] Shoeld, New Process Gives Improvement in Superphosphate Quality, *Chem. & Met. Eng.*, **41**, 178 (1934).

$$(CaF)Ca_4(PO_4)_3 + 7H_3PO_4 + 5H_2O \rightarrow 5CaH_4(PO_4)_2H_2O + HF$$

A considerable saving in freight and transportation costs is realized with this material; with phosphoric acid being produced in larger quantities and at cheaper prices, this product is being much more widely consumed than formerly.

If the rock used contains much organic material, this is first removed by heating to 1300°F. in a calcining furnace before crushing, in order to prevent fouling of the acid. Mixing of the rock with the phosphoric acid is usually done in a 2-ton acid phosphate mixer similar to that used for the sulfuric acid treatment in the den process. The action of phosphoric acid on the rock is *slower* than sulfuric acid and therefore several hours are required for the mixing. A partly concentrated acid, 62 per cent H_3PO_4, is usually chosen to help in controlling the moisture and drying requirements of the product. From the mixer, the wet material of about 20 per cent moisture content is transferred to the storage building where it is aged 30 to 40 days during which the moisture content drops somewhat. It is further artificially dried to only a few per cent moisture, by passing hot flue gases over the product, but care should be taken as the phosphate decomposes at a temperature above 200°C., which would increase the insoluble P_2O_5 content.

The material is conveyed by belts to a storage silo from which it is passed over a vibrating screen and the oversize is sent to a grinder. The finished product passes a 6-mesh screen and is conveyed to a dry-storage building ready for shipment. Triple superphosphate does not tend to take on water from the atmosphere under any humidity conditions. It is chemically entirely stable under commercial usages.

Ammoniated Superphosphates.—Consumers greatly prefer a fertilizer wherein the desirable plant nutrient constituents are incorporated into a product embodying chemical stability, uniformity in texture, and resistance to hygroscopic conditions for all normal storage and handling conditions. Ammoniation[1] of superphosphate produces a fertilizer with these desirable properties and supplies both phosphorus and nitrogen to the soil, but it is only recently that the cheap production of synthetic ammonia made this direct use in fertilizer mixtures containing superphosphate an economic accomplishment. Commercial production was first initiated in 1928. Instead of employing the gaseous ammonia or its aqueous solutions, many other ammoniation processes exist such as the mixing of ammonium sulfate or of ammonium nitrate with the superphosphate. However, there is enough acidity in the superphosphate to combine with or fix some ammonia. Formerly this acid partly destroyed the bags and made handling difficult. Some plants also utilize the NH_3 from waste coke-oven gases or other ammonia-containing gases by passing the gas over the superphosphate which absorbs the ammonia. Recent trends are toward the direct use of anhydrous liquid ammonia or liquid ammonia containing dissolved urea whereby the ammonia vapor pressure is reduced and organic nitrogen also added. Figure 2 depicts the adding of strong aqua ammonia to the aged superphosphate. A similar plant is used for liquid ammonia or the ammonia-urea liquor, omitting the solution tank.

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[1] HARDESTY and ROSS, Heat Developed in the Ammoniation of Superphosphates with Anhydrous Ammonia, *Ind. Eng. Chem.*, **29**, 1283 (1937).

Concentrated fertilizers[1] have also been developed to save the user transportation costs. Some of these contain up to 74 per cent total plant food and are also manufactured in pellets that are drillable and resist moisture.

Calcium Metaphosphate.[2]—Recently the T.V.A. has developed from phosphate rock a concentrated fertilizer, $Ca(PO_3)_2$, by the following reaction:

$$(CaF)Ca_4(PO_4)_3 + 3P_2O_5 + HPO_3 \rightarrow 5Ca(PO_3)_2 + HF$$

The procedures employed embody burning phosphorus with air and bringing these products of combustion into contact with lump rock in a vertical shaft, or blowing phosphate sands into the chamber where the phosphorus is being burned. The fluorine compounds may be recovered.

PHOSPHORUS

This element was first produced on a small commercial scale by treating calcined bone with sulfuric acid, filtering off the phosphoric acid, and evaporating it to specific gravity of 1.45. It was mixed with charcoal or coke, again heated, and the water evaporated off until the moisture content was less than 6 per cent. This mixture was placed in retorts and brought to white heat. The phosphorus was thus distilled off, collected under water, and purified by redistillation.

The production of phosphorus today still depends on the volatilization of the element from its compounds under reducing conditions. During the past decades, the method has changed chiefly in details and size of production. At the present time, elementary phosphorus is manufactured on a large scale as a heavy chemical and is shipped in tank cars from the point of initial manufacture, where the raw materials are cheap, to distant plants for its conversion to phosphoric acid, phosphates, and other compounds.

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[1] Klugh, Chemical Engineering Develops New Fertilizer Process, *Chem. & Met. Eng.*, **39**, 93 (1932).

[2] Copson, Pole, and Baskervill, Development of Processes for Metaphosphate Production, *Ind. Eng. Chem.*, **34**, 26 (1942); Easterwood, Recent Developments in the Phosphate Field, *Ind. Eng. Chem.*, **34**, 18 (1942) with bibliography.

Uses and Economics.—With the commercialization of cheaper methods for producing phosphorus on a large scale, widening fields for its own use and use of its compounds have been developed. Table 4 shows the amount of production of several of the more important commercial compounds of phosphorus in recent years. In addition to these compounds, hypophosphites, glycerophosphates, phosphorus chlorides, and phosphoric acid esters are quite important commercially. Channels of consumption for phosphorus derivatives other than as fertilizers may be divided into four chief groups: (1) food and medicine, (2) water treatment, (3) phosphate esters, and (4) miscellaneous uses.

The *food* uses include the important *medicinal* compounds of the glycerophosphates and the hypophosphites as well as the sodium and calcium phosphates. Pure calcium phosphate is a source of both calcium and phosphorus for man and animal. Many baking powders contain phosphates as their acid constituents. Sodium acid pyrophosphate and the acid orthophosphates of potassium, sodium, calcium, and ammonium have been used as such. The soft-drink industry buys tonnage quantities of pure acid to add a tartness to beverages. Victor Chemical Works and Monsanto Chemical Co. have been offering sodium ferric pyrophosphate, $Na_8Fe_4(P_2O_7)_5 \cdot xH_2O$, as an iron carrier in foods.

TABLE 4.—PRODUCTION OF CERTAIN PHOSPHORUS COMPOUNDS[a]

Compound	1941, short tons	1942, short tons	1943,[b] short tons
Phosphoric acid, 50 per cent H_3PO_4	661,504	617,269	628,695
Calcium phosphate, monobasic, $CaH_4(PO_4)_2 \cdot H_2O$	32,696	31,976	33,480
Sodium phosphate, monobasic, $NaH_2PO_4 \cdot H_2O$	8,255	10,467	10,753
Sodium phosphate, dibasic, $Na_2HPO_4 \cdot 7H_2O$	22,573	30,115	45,781
Sodium phosphate, tribasic, $Na_3PO_4 \cdot 12H_2O$	86,315	78,902	72,184

In addition there were produced about 50,000 tons of sodium pyrophosphate and miscellaneous amounts of calcium di- and tri-basic phosphates.

[a] *Chem. & Met. Eng.*, **51**, No. 2, 129–132 (1944).

[b] Estimated.

Water treatment[1] employs considerable quantities of phosphorus compounds as water softener, anticorrosion agents, and detergents in washing compounds. Trisodium phosphate has been extensively used, but sodium hexametaphosphate, sodium pyrophosphates, and sodium polyphosphates have recently become very important in this field because of both their good detergent qualities and their ability to retain calcium and magnesium ions in solution.

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[1] SCHWARTZ and MUNTER, Phosphates in Water Conditioning, *Ind. Eng. Chem.*, **34**, 32 (1942). This is a very excellent article with phase diagrams and a splendid bibliography. *Cf.* EASTERWOOD, *op. cit.*, p. 14.

Tricresyl, triphenyl, and tributyl phosphates are *organic esters* of phosphoric acid and are widely employed as plasticizers in the plastic and lacquer industries. The chief method of production of these is by the condensation of phosphorus oxychloride with the corresponding alcohol. Hundreds of organic derivatives of phosphorus may be found in literature but, as yet, only a very few are of commercial significance. With some research and development, these materials may open up entirely new and profitable fields in the future. Recently the alkyl esters of phosphoric acid have been studied[1] in detail by the Monsanto group and recommended for flameproofing cloth and paper (particularly the ammonium alkyl phosphates).

A seemingly infinite number of *miscellaneous*[2] uses may be mentioned for phosphorus and its derivatives, among which the following are important. Phosphorus enters the metallurgical fields as an alloying agent. Phosphorus and its compounds are constituents of match compositions. Phosphoric acid is being used to replace sulfuric acid as a petroleum refining agent and also as a catalyst for polymerizing olefins and for alkylating reactions. The acid is also employed with oxidizing agents as corrosion inhibitors and in rustproofing processes. Phosphates of sodium and ammonium are flameproofing reagents for wood and textiles. In fact it seems that in almost any industry that one might analyze, whether it be the leather, paper, brewing, cellulose, dye, printing, rubber, or soap industry, one is certain to find phosphoric acid used, or some other phosphorus derivative, in at least one step of the process.

MANUFACTURE OF PHOSPHORUS AND PHOSPHORIC ACID

Reactions.—Phosphorus has been produced by both the blast furnace and the electric furnace[3] methods. The following reaction is considered to take place, the raw materials being phosphate rock, silica, and coke:

$$2(CaF)Ca_4(PO_4)_3 + 9SiO_2 + 15C \rightarrow CaF_2 + 9CaOSiO_2 + 6P + 15CO$$

or more simply expressed,

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C \rightarrow 3CaSiO_3 + 2P + 5CO$$

The phosphorus is employed frequently as an intermediate product, being burned or oxidized to P_2O_5, which is dissolved in water to form the acids[1] or other compounds.

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[1] HOCHWALT, LUM, MALOWAN, and DYER, Alkyl Esters of Phosphoric Acid, *Ind. Eng. Chem.*, **34**, 20 (1942).

[2] EASTERWOOD, *op. cit.*, p. 18, bibliography.

[3] ZERGIEBEL and LUCAS, Phosphorus Furnace Reactions, *Trans. Electrochem. Soc.*, **81**, preprint (1942).

Phosphorus pentaoxide: $4P + 5O_2 \rightarrow 2P_2O_5$
Metaphosphoric acid: $P_2O_5 + H_2O \rightarrow 2HPO_3$
Pyrophosphoric acid: $P_2O_5 + 2H_2O \rightarrow H_4P_2O_7$
Orthophosphoric acid: $P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$

In addition, the old sulfuric acid or wet method is employed to manufacture phosphoric acid directly, by the reaction

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3(CaSO_4{\cdot}2H_2O)$$

The foregoing reactions are commercialized in the following sequences of *unit operations* (Op.) and *unit processes* (Pr.), as exemplified by Figs. 3 to 5:

Sulfuric Acid:	*Electric Furnace:*	*Blast Furnace:*
Phosphate rock ground and calcined (Op. and Pr.)	Phosphate rock ground (Op.)	Phosphate rock ground (Op.)
Ground rock reacted in mill with part of weak H_3PO_4 (Pr.)	Rock and sand mixed with coke and sintered, introduced into electric furnace (Op.)	Rock and coke briquetted, mixed with sand, charged to blast furnace (Op.)
Reaction continued in three agitators (Pr. and Op.)	Mix heated to reaction temperature (Pr.)	Reacted in furnace, using heated air (Pr.)
Reaction continued with rest of weak H_3PO_4 and with H_2SO_4 (Pr.)	Slag and ferrophosphorus run off (Op.)	Furnace gases through dust collector (Op.)
SiF_4 recovered (Op. and Pr.)	Phosphorus and CO drawn off, P condensed or oxidized with air (Pr.)	Part of P vapor burned in regenerator stoves (hot air) (Pr. and Op.)
Calcium sulfate filtered off and washed (Op.)	P_2O_5 cooled and hydrated (Op. and Pr.)	Rest of P vapor burned in steam boiler (Pr. and Op.)
This sludge pulped, refiltered, and rewashed (Op.)	Strong H_3PO_4 filtered and purified (Op. and Pr.)	All P_2O_5 hydrated (Pr.) 90 per cent H_3PO_4 collected (Op.)
Strong acid from first filter evaporated to stronger acid (Op.)		

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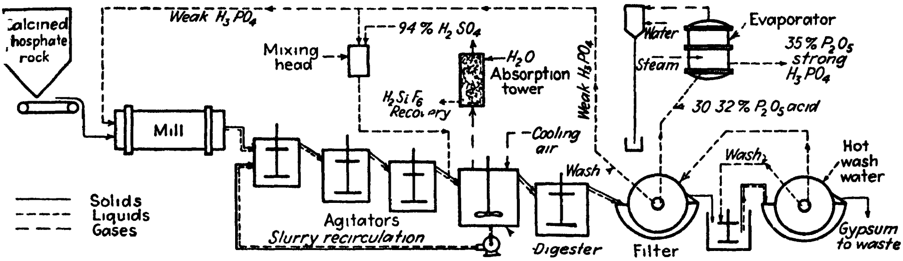
[1] DURGIN, LUM, and MALOWAN, The Chemical and Physical Properties of Strong Phosphoric Acids, *Trans. Am. Inst. Chem. Engrs.*, **33**, 643–668 (1937); *Chem. & Met. Eng.*, **44**, 721–727 (1937); CAROTHERS, Phosphoric Acid, 1918–1938, *Chem. Industries*, **32**, 523, 525, 527–528 (1938).

Sulfuric Acid or the Wet Method.—In the past, most of the phosphoric acid produced was prepared by the action of dilute sulfuric acid, 30°Bé., on ground phosphate rock or bones, but within the past few years this method has been improved. The Dorr strong-acid process[1] produces a stronger, cheaper, and purer acid. This follows the flow sheet of Fig. 3. The equipment should be lead lined, and sufficient time provided in the various agitators for the reaction to go to completion. The temperature in the digester should be kept low enough to ensure the precipitation of gypsum, $CaSO_4 \cdot 2H_2O$, and not anhydrite. If the latter is formed, it hydrates subsequently and causes plugging of pipes.



Phosphate rock (70 B PL)	2,350 lb	Per ton of 35% P_2O_5 acid
Sulfuric acid (94 %)	1,950 lb	
Water (Chiefly cooling)	7,500 gal	
Steam	780 lb	
Electricity	52 5 kw-hr	
Direct labor	0 8 man hr	

FIG 3.—Phosphoric acid by Dorr strong-acid process.

If the phosphoric acid is to be used for foods or pure chemicals, the acid should be purified from such impurities as silica, calcium sulfate, arsenic, iron, fluorine, aluminum, vanadium, or lead. Very often this purification is very difficult to effect. The procedure usually is to add finely ground limestone which causes precipitation of aluminum and iron phosphates, calcium fluoride, and fluosilicates. These may be removed by Oliver-type filters, or by means of a wooden plate-and-frame press. In some cases, the acid has a dark color, owing to the carbonization of organic matter in it, and it is often necessary to add some oxidizing agent as permanganate or chlorate to obtain a clear white acid. If this phosphoric acid is to be consumed for the manufacture of trisodium phosphate, its purity is suitable and it produces a very cheap product.

The concentration of the acid is usually brought about in lead-lined evaporators, containing lead steam coils. As the orthophosphoric acid is converted into pyrophosphoric acid when heated above 150°C., the concentration should be carried out with care. It is seldom considered practicable to produce an acid of higher concentration than 50°Bé. by

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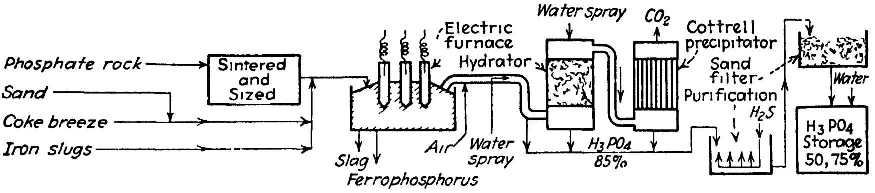
[1] WEBER, SHAFOR, and ROBERTS, Dorr Strong Acid Process, U.S. Pat., 2049032 (1936). PERRY, *op. cit.*, pp. 1644–1647, presents the c.c.d. practice still used in many plants; *ibid.*, p. 1691, for filter media.

this method; if it is done, the evaporation is usually carried out under vacuum.

Electric Furnace Method.—The electric furnace[1] was the first of the pyrolytic methods to be employed commercially (1920). The pyrolytic processes permit the use of lower grade rock than does the wet process as the slag carries off impurities. Indeed the lower grades are frequently preferred because of the better CaO to SiO_2 balance for slag formation. The principal requirement of the electric furnace method is cheap electricity.

The raw material, phosphate rock, is sintered or nodulized to facilitate escape of phosphorus vapors in the furnace and to prevent the blowing over of dust. After sintering, the material is sized and the fines returned to the sintering machine. Coke breeze and sand are added, and the materials charged to the electric furnace. Iron slugs are added to the charge if more ferrophosphorus is desired. A typical flow sheet with quantities required is shown in Fig. 4. The temperature of the furnace is approximately 2400°F. The electrodes are threaded on both ends so as to facilitate replacements as the carbon is consumed. The slag from the furnace is usually tapped periodically and is crushed for use as aggregate for road construction or in concrete. The ferrophosphorus runs out with the slag, is separated, and sold.



Phosphate rock (698 BPL)	3,970 lb	Iron (depends on ferrophosphorus requirements		Per ton 85% H_3PO_4
Silica rock	1,270 lb	Electricity	3,460 kw-hr	
Coke breeze	748 lb	Direct labor	(est) 05-1 man-hr	

FIG. 4.—Phosphoric acid flow sheet. Electric furnace process by one-step system.

The gases from the furnace containing P and CO are withdrawn by means of a fan. In some plants, air is admitted here, and the phosphorus is burned directly to P_2O_5 in what is known as the *one-step* system. This results in a large wastage of the CO. The *two-step* method is the better unless the local market is for phosphoric acid. In the two-step method the gases are cooled, and the condensed phosphorus is collected unde water and transported in tank cars to consumption centers where *it* is burned in a separate step. This method permits the use of the CO as fuel. The large plants of Victor and of Monsanto in Tennessee manufacture and ship phosphorus[1] in tank cars or drums.

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[1] CURTIS, The Manufacture of Phosphoric Acid by the Electric Furnace Method, *Trans. Am. Inst. Chem. Engrs.*, **31**, 278 (1935); CURTIS and MILLER, Operating Observations at T.V.A. Fertilizer Works, *Chem. & Met. Eng.*, **43**, 408 (1936), CURTIS, MILLER, and JUNKINS, T.V.A. Estimates Favorable Costs for Concentrated Superphosphate, *Chem. & Met. Eng.*, **43**, 583–587, 147 (1936); CURTIS, MILLER, and NEWTON, Process Development at T.V.A. Phosphoric Acid Plant, *Chem. & Met. Eng*, **45**, 193 (1938), useful diagrams. PERRY, *op. cit.*, p. 2815, tabulates some of the essential furnace conditions.

In the one-step system, as practiced[2] by the T.V.A., the furnace gases are usually burned in a tall packed tower with a water spray to form the phosphoric acid. The gases from the tower are passed through a Cottrell precipitator to remove any remaining phosphoric acid. The chief difficulties to overcome in this method are the formation of the meta acid by reaction with the moisture in the air, which results in plugging up the flues and fouling the fan, and the corrosion caused by both the P_2O_5 and the acid formed. Phosphorus pentaoxide is very corrosive toward most refractories, especially at high temperatures. The acid is usually purified with respect to arsenic by passing in H_2S as shown in Fig. 4, or by adding some soluble sulfide and filtering out the precipitated sulfides. If the acid is to be used in the manufacture of the triple superphosphate, it need not be purified.

Blast Furnace Method.—The first patent on the blast furnace[3] for making phosphorus was issued in France in 1867 and, at the time, was not considered practicable. Little was done about it for the next 30 or 40 years, and it was not until 1929 that commercial production by this process actually was successfully put into practice. The blast furnace used is similar in appearance to that employed in the steel industry. The last blast furnace operated was approximately 95 ft. high and had a maximum capacity of 250,000 lb. P_2O_5 per day. This has been shut down since 1939 but some engineers expect to see this process started again using air blast enriched as to its oxygen content.

The phosphate rock used was pulverized and mixed with the reduction carbon which was in the form of ground coke. A binder was added and the rock was compressed into briquettes which were dried to a moisture content of less than 1 per cent and stored. A car on tracks carried the briquettes to the top of the furnace where they were dumped in along with the silica gravel (see Fig. 5 for the flow sheet). The slag consisted chiefly of calcium silicate, contained only 2 per cent P_2O_5, and was tapped from the furnace every hour. The gases left the furnace and passed through a dust catcher, a series of cyclone dust collectors, and special fume collectors. The cleaned gas stream was then split three ways, one portion going to the phosphorus condensing plant (not shown in the figure), a second portion passing into special boilers for steam generation, and the third burning in the hot regenerative stoves for heating the furnace air blast. The P_2O_5 in the gaseous products of combustion from the boilers and stoves was led into hydrating chambers where cooling and hydration took place. The cooled gases from here were fanned to Cottrell electrical precipitators where any entrained liquid phosphoric acid was condensed (85 to 90 per cent H_3PO_4). The phosphorus volatized from the rock over a year averaged as high as 95 per cent, and the P_2O_5 yield was above 90 per cent of that charged. Arsenic, the chief impurity of the acid prepared by this method, was removed by adding H_2S and filtering.

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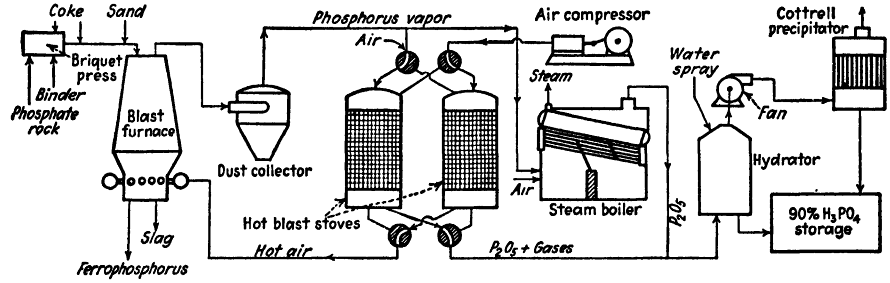
[1] KIRKPATRICK, Phosphorus for Progress, *Chem. & Met. Eng.*, **44**, 644 (1937).

[2] See references by Curtis, *et al.*, and the pictured flow sheet in *Chem. & Met. Eng.*, **46**, 269 (1939).

[3] EASTERWOOD, Making of Phosphoric Acid in the Blast Furnace, *Chem. & Met. Eng.*, **40**, 283–287 (1933); *Trans. Am. Inst. Chem. Engrs.*, **28**, 1 (1933). Pictured flow chart, *Chem. & Met. Eng.*, **46**, 269 (1939).



Phosphate rock (27% P_2O_5)	6,000 lb.	Air	450,000	cu.ft.	100% H_3PO_4
Silica sand	1,500 lb.	Water (total)	75,000	gal.	
Coke	7,000 lb.	Electricity*	4	kw-hr	
Briquet binder	500 lb.	Direct labor	2-4	man-hr.	

*For precipitation only; electricity for power depends on waste heat recovery

FIG. 5.—Phosphoric acid flow sheet—blast furnace process.

Corrosion[1] difficulties are quite serious in handling phosphoric acid. Rubber-lined tank cars are usually employed for transporting it in large quantities. Lead may be used in contact with cold concentrated phosphoric acid but fails at higher temperatures. In one plant lead-lined steel pipe has been replaced by Duriron. Rubber hose is also widely used. The attack on lead seems to be due especially to the P_2O_5 and gases evolved from strong acid. Warm, concentrated H_3PO_4 may be satisfactorily handled by cast molybdenum stainless steels having a low C content and containing Cr and Ni. This alloy seems to be the best of all, though vanadium alloys are also used. Wood may be employed for solutions up to 10 per cent and up to 70°C. Paraffined wood is adapted to some cases. Stoneware and high-silica acid-resisting bricks and cement are quite resistant and are employed in the construction of tanks. Often the tanks are made of concrete, lined with several layers of asphalt and tar paper, then with chemical lead, and finally with acidproof masonry. For the filter presses, a new cloth has been developed that is successful for acids of 35 per cent P_2O_5 and temperatures of 70°C. It is a special long-staple cotton nitrated after weaving. Synthetic resins and enamelware also are finding uses in the phosphoric acid industry.

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[1] WEBER, Phosphoric Acid Imposes Severe Corrosion Burdens, *Chem. & Met. Eng.*, **39**, 542–545 (1932).

SODIUM PHOSPHATES

Although trisodium phosphate has long been an important article of commerce (Table 4), in the past decade much research has been done on the alkali metal salts of the *various* phosphoric acids. As a result, a number of new and very useful salts have been manufactured and introduced to commerce.[1] The industrially important sodium phosphates may be classified:

Alkali metal *metaphosphates*, such as $NaPO_3$, sodium metaphosphate, and sodium hexametaphosphate, $(NaPO_3)_6$, or Graham's salt.

Alkali metal *polyphosphates*, such as $Na_5P_3O_{10}$, sodium tripolyphosphate.

Alkali metal *pyrophosphates*, such as $Na_4P_2O_7 \cdot 10H_2O$, sodium or tetrasodium pyrophosphate.

Alkali metal *orthophosphates*, such as $NaH_2PO_4 \cdot H_2O$, $Na_2HPO_4 \cdot 7H_2O$, and $Na_3PO_4 \cdot 12H_2O$.

The first three groups may be looked upon as molecularly dehydrated from the orthophosphates. The alkali metal polyphosphates[2] are of rather indefinite molecular composition and are frequently included among the phosphate glasses, which also may embrace sodium metaphosphates, Graham's salt.

The development of these various molecularly dehydrated phosphates, with a range of properties particularly directed toward conditioning water, was stimulated, if not started, by the work of R. E. Hall[3] and his associates of the Hall Laboratories. Water varies so much in its impurities and its pH that softening agents are needed of the varying properties of phosphates, from the strongly alkaline Na_3PO_4 through all ranges to the strongly acid NaH_2PO_4. However, in water softening, the behavior toward the deleterious constituents, calcium, magnesium, iron, and aluminum, is of the most importance and, although Na_3PO_4 precipitates insoluble phosphates or hydroxides usually of a loose form and hence easily removable, yet the newly discovered properties of metaphosphates, polyphosphates, and tetraphosphate in solubilizing or *repressing* the calcium and magnesium precipitates, even *in presence of soaps*, are of the utmost industrial significance. Such action takes place by binding, for example, the calcium and magnesium into such complexes as $Na_2(Ca_2P_6O_{18})$ and $Na_2MgP_2O_7$.

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[1] EASTERWOOD, Recent Developments in the Phosphate Field, *Ind. Eng. Chem.*, **34**, 13 (1942), with excellent bibliography; SCHWARTZ and MUNTER, *op. cit.*, a most excellent article with charts to summarize the properties of the various phosphates; LOGUE, The Family of Phosphates, *Chem. Industries*, **49**, 302 (1942), with tabulation of uses of phosphates.

[2] PARTRIDGE, HICKS, and SMITH, A Thermal Microscopic and X-ray Study of the System $NaPO_3$-$Na_4P_2O_7$, *J. Am. Chem. Soc.*, **63**, 454–463 (1941).

[3] HALL, U.S. Pat., 1956515 (1934), Reissue 19719 (1935).

The molecularly dehydrated phosphates supplement the long-known orthophosphates in practical water treatment by being able:[1]

1. To provide acid, neutral, or alkaline solutions for control of pH value by both neutralization and buffer action.
2. To act as emulsifying agents.
3. To reduce metal-ion concentration by precipitation.
4. To reduce metal-ion concentration by complex formation.
5. To reduce alkalinity by hydrolysis to orthophosphate.
6. To stabilize solutions supersaturated with respect to ordinarily insoluble salts.
7. To form adsorbed films on metal surfaces.
8. To disperse insoluble compounds through adsorption on the solid particles.

Metaphosphates.—Under this head is included the soluble sodium hexametaphosphate, $(NaPO_3)_6$, which is made by fusing NaH_2PO_4 to approximately 760°C. and quickly cooling. This finds wide employment in water treatment. An insoluble low-temperature (350 to 400°C.) metaphosphate is the dentifrice in a widely sold toothpaste. The T.V.A. group[2] have studied and produced many thousand tons of metaphosphates chiefly for fertilizers. Calcium and potassium metaphosphate with 71.7 per cent and 60.1 per cent P_2O_5, respectively, in the pure compounds offer savings in transportation and handling charges. Reactions involved may be expressed:

$$NaH_2PO_4 \rightarrow NaPO_3 + H_2O$$
$$Ca_3(PO_4)_2 + 2P_2O_5 \rightarrow 3Ca(PO_3)_2$$
$$KCl + HPO_3 \rightarrow KPO_3 + HCl$$

Of the *polyphosphates* the only definitely crystalline member is sodium tripolyphosphate, $Na_5P_3O_{10}$.

To produce the sodium tripolyphosphate[3] a definite temperature control is necessary. When mono- and disodium phosphates in correct proportions or equivalent mixtures of other phosphates are heated for a substantial time between 300 and 500°C. and slowly cooled, the product will practically all be in the form of the tripolyphosphate. If, however, the mixture is fused and rapidly cooled, the product will be substantially a mixture of meta- and pyrophosphates. This mixture may be converted to the tripolyphosphate by reheating and tempering at a temperature above 300°C. but below the fusion point.

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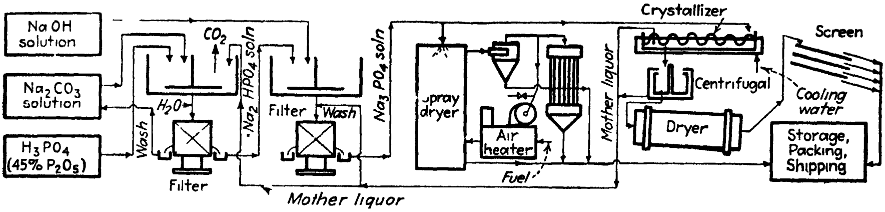
[1] Quoted from Schwartz and Munter, *op. cit.*, p. 36.

[2] COPSON, POLE, and BASKERVILL, Development of Processes for Metaphosphate Productions, *Ind. Eng. Chem.*, **34**, 26–32, (1942).

[3] EASTERWOOD, *op. cit.*, p. 15; *cf.* SCHWARTZ and MUNTER, *op. cit.*, particularly for application.

The chemical properties of the alkali metal tripolyphosphates would appear to place them somewhere between pyro- and metaphosphates, having less calcium and more magnesium repressing value than the metaphosphates, and more calcium and less magnesium repressing value than the pyrophosphates.

All these molecularly dehydrated phosphates, especially metaphosphates and polyphosphates but also to a less extent the pyrophosphates, are useful for water treatment. The steam boiler comes first to mind, but the application of these water-conditioning compounds is just as important in all washing and cleaning whether in the home or in the large woolen or cotton mill.



Phosphoric acid (45% P_2O_5)	880 lb	Per ton of $Na_3PO_4 \cdot 12H_2O$
Na_2CO_3 (58% Na_2O)	600 lb	
Na OH (76% Na_2O)	240 lb	
Steam	150 lb	
Electricity	80 Kw-hr	
Direct labor	8 man hr	

FIG. 6.—Flow sheet for trisodium phosphate

Sodium pyrophosphate[1] is $Na_4P_2O_7 \cdot 10H_2O$, an old compound made by dehydration of disodium phosphate in a rotary kiln.

$$2Na_2HPO_4 \rightarrow Na_4P_2O_7 + H_2O$$

Only recently has this compound been extensively adopted as a component of soap powders to save, in many hard waters, 20 to 30 per cent of the soap by solubilizing or repressing the precipitation of the magnesium and part of the calcium soaps. A nonhydroscopic acid sodium pyrophosphate, used in baking powder formulation, is manufactured by heating monosodium phosphate to a temperature between 225 and 250°C. over the course of 6 to 12 hr.

$$2NaH_2PO_4 \rightarrow Na_2H_2P_2O_7 + H_2O$$

Calcium acid pyrophosphate also is employed in commercial baking powders.

Trisodium phosphate, $Na_3PO_4 \cdot 12H_2O$, is used in industry because of its two chief properties: (1) It is hydrolyzed in a water solution to give a high pH solution well buffered against neutralization. (2) It possesses the ability easily to form soft and granular precipitates with heavy metal ions such as magnesium, iron, aluminum, and calcium. Trisodium phosphate has been by far the most important compound of phosphoric acid used as a water softener and detergent, and its production has increased. But new sodium salts of the molecularly dehydrated phosphates have partly replaced trisodium phosphate in water treatments. Trisodium phosphate is employed in the leather industry for treating hides, in the steel industry to inhibit steel corrosion, as a paint remover, in boiler treatment, as a radiator cleanser, and as an emulsifying agent. It is very useful for degreasing and degumming in the metallurgical industries and for deodorizing and cleansing.

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[1] EASTERWOOD, *op. cit.* pp. 15, 19, bibliography.

Its manufacture must be carried out in two steps:

$$Na_2CO_3 + H_3PO_4 \rightarrow Na_2HPO_4 + CO_2 + H_2O$$
$$Na_2HPO_4 + NaOH \rightarrow Na_3PO_4 + H_2O$$

The procedure[1] as depicted in the flow sheet of Fig. 6, is as follows: 6,000 lb. of 58 per cent soda ash are introduced into a 4,000-gal. tank with 800 gal. of hot liquor from previous crystallization of $Na_3PO_4 \cdot 12H_2O$; 8,800 lb. of phosphoric acid solution, containing 45 per cent P_2O_5, are added at the surface of the tank so that CO_2 can be liberated easily. A slight excess of soda ash is added and the solution is boiled by steam until all of the CO_2 has been driven out as confirmed by the test sample. Since the pH level at which the third H of the acid is neutralized is higher than that at which the second H of carbonic acid is converted to form sodium carbonate, it is not to be expected that H_3PO_4 can be neutralized further than to the disodium stage with sodium carbonate. The disodium phosphate solution is filtered in a plate-and-frame filter press at 85 to 100°C., and the filtrate is pumped to storage tanks or to the trisodium process tank. This clear solution of disodium phosphate contains 14.5 per cent P_2O_5 and 13 per cent Na_2O. The small amount of white mud (Fe and Al phosphates plus SiO_2) in the press is wasted.

Fifteen hundred gallons of hot disodium phosphate solution is changed to trisodium phosphate, in a 4,000-gal. iron tank, by adding 2,800 lbs. of caustic soda in 300 gals. of water at 90°C.; an additional 1,000 gal. of disodium phosphate solution is then added. Samples are titrated to control this operation. The hot solution of trisodium phosphate is filtered and passed to Swenson-Walker crystallizers. The crystals are dried in a centrifuge, further dried in a rotary drier, cooled, screened, and aged for 3 or 4 days by storage in piles. A spray congealed grade is also produced by pumping a clear filtered solution of Na_3PO_4 to the top of a spray tower 70 ft. high where an atomizer discharges it. During the fall of 70 ft. countercurrent to hot air, the particles assume a spherical form and congeal.

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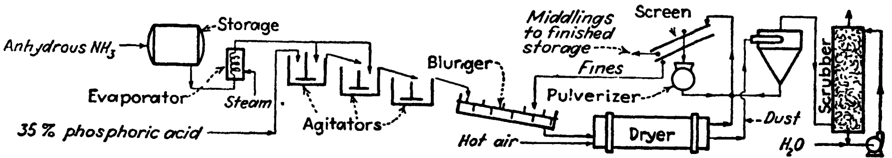
[1] SNELL, Trisodium Phosphate—Its Manufacture and Use, *Ind. Eng. Chem.*, **23**, 470 (1931).

New processes for trisodium phosphate manufacture include a thermal one in which soda ash or caustic is fused with apatite, and also a wet process in which finely ground apatite is lixiviated with caustic liquors. Neither process is in commercial production as yet. Should production difficulties be solved, these two processes should supplant the phosphoric acid neutralization process, because of the cheapness of available phosphorus pentaoxide in apatite as compared with phosphoric acid.

Trisodium phosphate has been produced by sintering, in a rotary kiln, a mixture of finely ground ferrophosphorus and soda ash in the presence of air. The sinter is leached with water to remove the soluble trisodium phosphate which is then crystallized, centrifugated, and dried. The iron is recovered as an oxide residue.

AMMONIUM PHOSPHATES

The monoammonium phosphate, $NH_4H_2PO_4$, and the diammonium phosphate, $(NH_4)_2HPO_4$, are both manufactured commercially. The monoammonium phosphate is made simply by passing ammonia gas into 75 per cent H_3PO_4. Considerable heat is given off in the reaction, and the mass becomes pasty and crystallizes to an almost solid mass on cooling. The white crystals are centrifuged free from the mother liquor and dried for sale.



Ammonia	280 lb.	Per ton of ammonium phosphate
Phosphoric acid (35%)	2,850 lb	
Dryer fuel	2,000,000 B.t.u.	
Electricity	13 kw-hr	
Direct labor	0.7 man-hr.	

FIG. 7.—Flow sheet for diammonium phosphate.

The production of the diammonium salt is brought about by conducting ammonia into 35 per cent acid with agitation as shown in the flow sheet of Fig. 7. After passing through a series of agitating tanks and a blunger, the product is dried, screened, and crushed for size. The excess ammonia is scrubbed out of the gas in a scrubbing tower. A more dilute acid, such as the 35 per cent H_3PO_4 of the flow sheet, should be used in the *di* salt preparation to prevent operating difficulties. If the acid employed is too concentrated, the rise in temperature caused by the heat of the reaction will be so great that the solution will no longer take up any more ammonia, resulting in a mixture of the mono- and diammonium salts. If the mixture is cooled at this point, the mass solidifies, which *also prevents any further absorption of ammonia to convert the product* to the diammonium phosphate.

The principal uses of ammonium phosphate are as an ingredient of fireproofing agents for woods and fabrics and as a source of plant food in fertilizer.

BAKING POWDERS

The baking powder industry is believed to be the second most important consumer of phosphate rock, being surpassed only by the fertilizer industry. The use of leavening agents to produce aeration and lightness in breads and cakes has been known since the time of the Egyptians and handed down through the Greeks and Romans. Leavened and unleavened bread are both mentioned in the Bible. Some form of yeast or ferment acting on the carbohydrates of the flour giving CO_2 and an alcohol was the first of the leavening agents used. Later, baking soda, sodium bicarbonate, was widely used but, because it often imparted an unpleasant taste or even a yellowish color due to the alkalinity of the Na_2CO_3 formed, the search for better reagents continued.

The present-day baking powders consist of a dry mixture of sodium bicarbonate with one or more chemicals capable of completely decomposing it, such as the acid salts of phosphoric acid, sodium and potassium acid sulfates, alum, tartaric acid, or the acid tartrates. A filler or drying agent, such as starch or flour, is frequently added to the active ingredients to give a better distribution throughout the dough and to act as a diluent or preventive of the reaction until water and heat are applied.

The use of acid phosphates has constantly become more important. This may be attributed to the fact that these may be produced at a relatively low cost and that phosphorus compounds are believed to help the growth of bone and tissue, although usually present in only small amounts. The production of the various baking powders is understood to be over 160,000,000 lb. per year. Monocalcium phosphate, $CaH_4(PO_4)_2 \cdot H_2O$, and monosodium phosphate, NaH_2PO_4, are the chief phosphate compounds used for baking purposes. When mixed with $NaHCO_3$ and a diluent and filler such as cornstarch or flour, the product is often known as a straight phosphate baking powder. Sodium acid pyrophosphate makes a slow-acting baking powder. Calcined alum, $Na_2SO_4 \cdot Al_2(SO_4)_3$, is often added to the sodium bicarbonate to produce slower acting baking powders which react but slightly in the cold, but more vigorously when heated.

The following equations represent the actions of the different baking powders:

$$Na_2Al_2(SO_4)_4 + 6NaHCO_3 \rightarrow 6CO_2 + 4Na_2SO_4 + 2Al(OH)_3$$
$$3CaH_4(PO_4)_2H_2O + 8NaHCO_3 \rightarrow 8CO_2 + Ca_3(PO_4)_2 + 4Na_2HPO_4 + 11H_2O$$
$$KH_2PO_4 + NaHCO_3 \rightarrow CO_2 + KNaHPO_4 + H_2O$$
$$NaH_2PO_4 + NaHCO_3 \rightarrow CO_2 + Na_2HPO_4 + H_2O$$
$$Na_2H_2P_2O_7 + 2NaHCO_3 \rightarrow 2CO_2 + 2Na_2HPO_4 + H_2O$$
$$KHC_4H_4O_6 + NaHCO_3 \rightarrow KNaC_4H_4O_6 + CO_2 + H_2O$$

In the United States, baking powders must yield not less than 12 per cent available CO_2, and most powders are so made up that they contain from 26 to 29 per cent $NaHCO_3$ and enough of the acid ingredients to decompose the bicarbonate and yield from 14 to 15 per cent CO_2. The rest of the powder, 20 to 40 per cent, consists of cornstarch or flour.

Though the manufacture of baking powders may seem quite simple, considerable skill and experience are essential for their successful commercial production and keeping. The Federal Food and Drug Acts permit the use of only pure and harmless materials, and competition in the industry is so great that even the slightest discoloration of the product may seriously decrease its sale.

In the manufacture of *monocalcium phosphate*, hydrated lime is mixed with enough phosphoric acid to convert nearly all of the lime to the phosphate without having excess acid. The reaction mass is stirred and considerable heat is given off, resulting in the evolution of steam. When the reaction mass begins to set, it is dumped on the floor for further drying and to complete the reaction. This takes from 12 to 18 hr. longer. The lumps of the acid phosphate are fed to a vacuum steam-heated drier where all but 1 per cent moisture is removed. The product is ground, screened, and mixed with other ingredients to fulfill baking powder requirements.

Of the acid phosphates used, monosodium and potassium phosphates are hydroscopic, while the sodium acid pyrophosphate and the monocalcium phosphate are not. Recently an improved and surface-coated anhydrous monocalcium phosphate has been introduced[1] for baking powder use. This is manufactured by reacting strong phosphoric acid with lime in the presence of certain minor materials as a potassium salt which, after the formation of the anhydrous $Ca(H_2PO_4)_2$ at 140 to 175°C., are caused to form a glassy coating by heating to 200 to 220°C. This coated anhydrous dicalcium phosphate used in a baking powder resists decomposition in presence of $NaHCO_3$ and moisture. This property prevents any appreciable loss of leavening gas in the dough-mixing step. The result is that the baked products have a larger volume.

[1] EASTERWOOD, *op. cit.* p. 15.

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CHAPTER XIX

SULFUR AND SULFURIC ACID

One of the most important and basic raw materials in the chemical process industries is sulfur. It exists in nature both in the free state and combined in ores such as pyrite, FeS_2. The mining of sulfur in Louisiana and Texas by the Frasch process, with the production of single blocks of pure sulfur ¼ mile long and over 50 ft. high, is a large and essential industry. Beside its most important application in the manufacture of sulfuric acid, sulfur is used extensively in explosives, refrigerants, rubber, pulp, and paper. The avenues of consumption are shown in Table 1.

Historical.—Sulfur has a history as old as any other recorded and has developed from a mystic yellow of the alchemist to one of the most useful substances in modern civilization. It was burned in early pagan rites to drive away evil spirits, but even then the fumes were used as a bleach for cloth and straw.

For many years a French company held a monopoly on elemental sulfur by controlling the world production from mines in Sicily. Partly for this reason and partly because of the abundance of pyrite, sulfur itself was little used prior to 1914. Though sulfur was discovered in the Gulf region of the United States by oil prospectors in 1869, it was difficult to mine because of overlying beds of quicksand. Before 1914 the United States made most of its sulfuric acid from imported and domestic pyrite and by-product sulfur dioxide from copper and zinc smelters. The mining of sulfur in Texas and Louisiana by the Frasch process was increased around 1914 to offset the shortage of imported pyrite due to war conditions. The new sulfur wells were not completed in time to participate in the war markets, but they were able to continue and expand because the use of elemental sulfur had been found advantageous in comparison with imported pyrite.

Uses and Economics.[1]—Production of elemental sulfur in the United States in 1939 was 2,090,979 long tons, of which about 80 per cent came from Texas and most of the rest from Louisiana. This constituted about 90 per cent of the world production. In 1939, there were obtained from the purification of fuel gas 4,307 long tons of sulfur and 13,000 long tons of hydrogen sulfide. These amounts have been increased. From sulfide concentrates of copper and zinc ores, 687,176 short tons of 60° Bé. sulfuric acid was made. In the United States in 1939, chiefly from Tennessee, 511,739 long tons of pyrite were mined. In 1939 from Spain and Canada 482,336 long tons of pyrite were imported. Table 1 lists the relative consumption of sulfur in the United States in 1940 and 1941.

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[1] Duecker and Eddy, Sulfur's Role in Industry, *Chem. Industries*, **50**, 174 (1942).

TABLE 1.—CONSUMPTION OF SULFUR
(In long tons)[a]

	1940	1941
Chemicals......	800,000	1,060,000
Fertilizer and insecticides	410,000	450,000
Pulp and paper	320,000	360,000
Explosives.......	74,000	83,000
Dyes and coal-tar products	51,000	65,000
Rubber..	47,000	55,000
Paint and varnish	54,000	65,000
Food products	6,000	6,000
Miscellaneous .	86,000	95,000
Totals.	1,848,000	2,239,000

[a] "Minerals Yearbook," 1941, U.S. Bureau of Mines. For 1943, *Chem. & Met. Eng.*, **51**, No. 2, 112 (1944) estimates a domestic sulfur consumption of 3,070,000 long tons, of which half was consumed in making sulfuric acid.

MINING AND MANUFACTURE OF SULFUR

Sulfur is obtained as elemental sulfur from sulfur dioxide and from hydrogen sulfide. Pure sulfur is mined but the sulfur dioxide comes from the roasting of sulfide ores and the hydrogen sulfide is removed from industrial gases.

Frasch Process.—Ninety per cent of all the elemental sulfur of the world is obtained from the sulfur-bearing porous limestones in the salt-dome cap rocks of Texas and Louisiana by the Frasch process.[1] As early as the late 1890's, Herman Frasch devised the following ingenious method of melting the sulfur underground and of pumping it up to the surface: Ordinary oil-well equipment is used to bore holes to the bottom of the sulfur-bearing strata, a distance underground of from 500 to 1,500 ft. A nest of three concentric pipes, varying in size from 6 in. to 1 in., is slipped down the well casing. The outside pipe of this nest, 6 in. in diameter, passes through the sulfur-bearing stratum and rests on the upper portion of the barren anhydrite, as shown in Fig. 1. A 3-in. pipe passes through the 6-in. one so that an annular space exists between the

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[1] A pictured flow sheet of the Frasch procedure is given in *Chem. & Met. Eng.*, **48**, No. 3, 104 (1941). For a fuller account of sulfur, the following should be consulted: Haynes "The Stone That Burns," D. Van Nostrand Company, Inc., New York, 1942; Duecker, Sulfur and National Defense, *Chem. & Met. Eng.*, **48**, No. 3, 70 (1941); Sulphur, an Essential to Industry and Agriculture, 45 pp., Texas Gulf Sulphur Co., New York, 1940; Modern Sulphur Mining, 27 pp., *ibid.*, 1941.

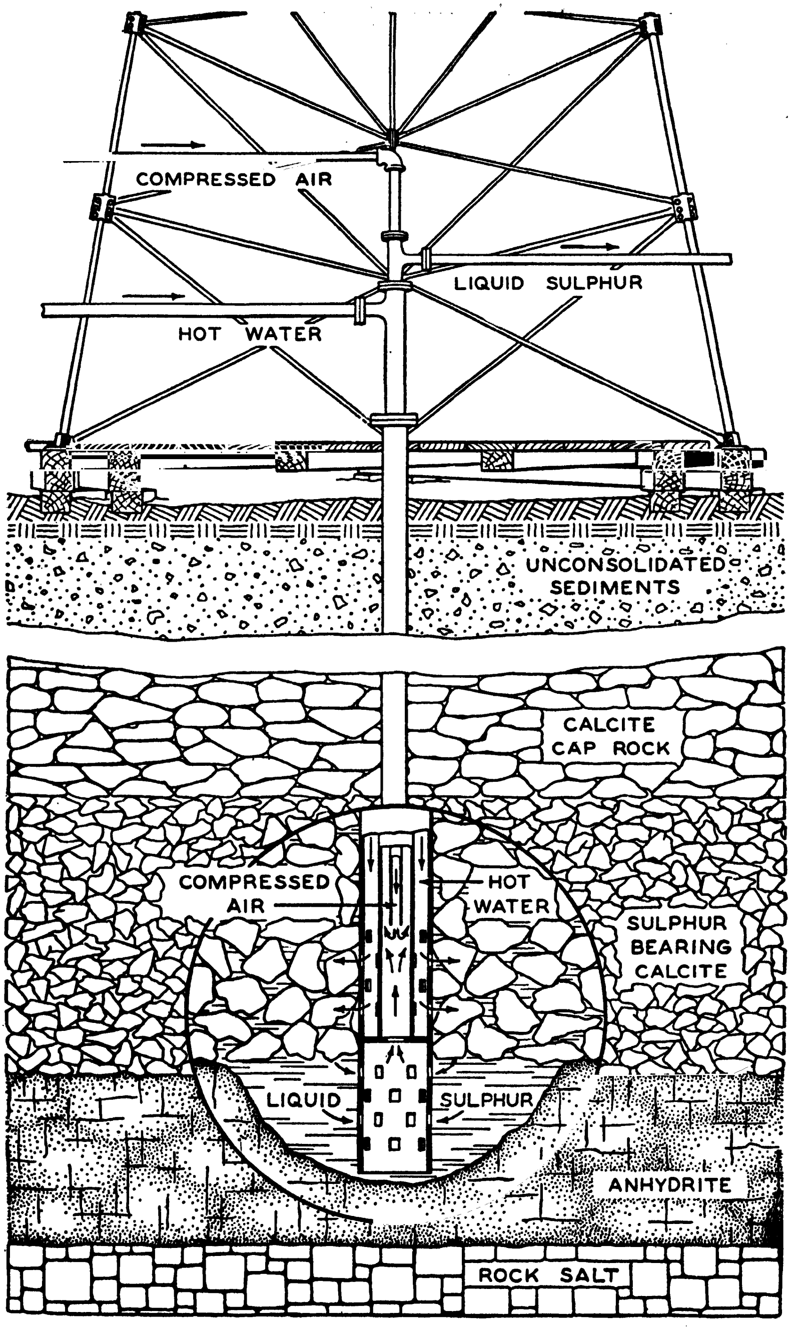

Fig. 1.—Sulfur-well piping. (*Courtesy of Texas Gulf Sulphur Company, Inc.*)

two, extends nearly to the bottom of the sulfur-bearing rock, and rests on a collar that seals the annular space between the 6-in. and the 3-in. pipes. An air pipe, 1 in. in diameter, inside the others, reaches to a depth slightly above the collar mentioned above. The 6-in. pipe is perforated at two different levels, one above and the other below the annular collar. The upper set of perforations permits escape of the hot water while the molten sulfur enters the system through the lower perforations.

For operation of the well, hot water at above 330°F. is passed down the annular space between the 6-in. and the 3-in. pipes. It discharges through the perforations into the porous formation near the foot of the well. The sulfur-bearing rock about the well through which this water circulates is raised to a temperature above the melting point of sulfur, 235°F. Molten sulfur, being heavier than water, sinks to form a pool around the base of the well where it enters through the lower perforations and rises in the space between the 3-in. and the 1-in. pipes, as depicted in Fig. 1. The height to which the sulfur is forced by the pressure of the hot water is about halfway to the surface. Air, compressed to 500 lb. at the pump house and at the bottom of the central 1-in. pipe, rises and mixes in the sulfur column in the 3-in. pipe, thus producing an air lift that raises the sulfur to the surface. At the surface, the sulfur from the wells is collected in steam-heated sumps at pumping stations from which it is pumped through pipes heated by an inner steam pipe into large storage vats where the sulfur solidifies. The block of sulfur is drilled, broken down by blasting, and loaded into cars by a locomotive crane.

It is far-sighted business to maintain a large supply of sulfur aboveground sufficient for over a year, because the production of sulfur may be seriously curtailed or entirely stopped for months at a time because of underground movements following the sulfur removal.

Sulfur from Sulfur Dioxide.—At Trail, B.C., the smelter produces a very large amount of sulfur dioxide from the roasting of the lead, zinc, and iron sulfides. Although 600 tons per day of 100 per cent sulfuric acid are made, much of the sulfur would still be unused if it were not for a recent chemical engineering development that converts this sulfur dioxide into free sulfur. In 1938, about 200 tons of sulfur per day[1] were produced. The sulfur recovery process, in essence, consists merely in the absorption of the dilute sulfur dioxide from the roaster gases in ammonium sulfite solution from which it is eliminated as 100 per cent sulfur dioxide by treatment with concentrated sulfuric acid. The pure sulfur dioxide is reduced by incandescent coke to a crude sulfur which is readily refined to yield the 99.99 per cent brimstone of commerce.

Sulfur from Industrial Gases.—Hydrogen sulfide is removed in the purification of coke-oven gas, water gas, refinery-still gas, natural gas, and other fuel gases. Either hydrogen sulfide or free sulfur is the by-product, depending on the recovery process. In all processes the hydrogen sulfide is absorbed or adsorbed by chemicals but, in at least one case, the absorbing agent is regenerated by oxidizing the H_2S to elemental sulfur; in another, the H_2S is liberated directly.

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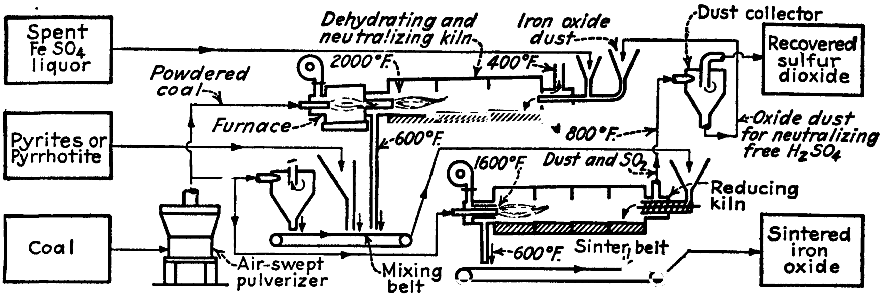
[1] KIRKPATRICK, Trail Solves Its Sulfur Problem, *Chem. & Met. Eng.*, **45**, 492 (1938).

Descriptions of these sulfur recovery systems are presented in Chap. VII. The hydrogen sulfide thus produced may be burned in specially constructed furnaces to form sulfur dioxide[1] for sulfuric acid. From these gases, there are recovered each year over 30,000 tons, expressed as elemental sulfur.



Spent $FeSO_4$ liquor (containing 26 tons H_2SO_4, 49 tons $FeSO_4$)	300 tons	Coal	45 tons	Per 100 tons recovered SO_2
Pyrite	80 tons	Electricity	2,900 kw-hr.	
		Labor	96 man-hr.	

FIG. 2.—Sulfur dioxide recovery from waste ferrous sulfate.

Sulfur Dioxide from By-products.—In the United States, a very large amount of ferrous sulfate is wasted into the streams, this coming mostly from steel pickling plants. It has been estimated that this pickle liquor amounts to over 500,000 gal. per day with an approximate composition of 5 to 6 per cent sulfuric acid and 20 per cent $FeSO_4$. This would be equivalent to about 500 tons of sulfuric acid per day. Much work has been done upon recovery of the values of the pickling liquors.[2] The flow sheet of Fig. 2 outlines the sequences of unit processes and unit operations whereby this, a ferrous sulfate liquor from a titanium dioxide plant at Sayreville, N.J., is converted into sulfur dioxide with Fe_2O_3 as a by-product. The main reactions may be represented as follows:

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[1] CRAISE and BROWN, Oil Refinery Hydrogen Sulfide Found to Be Economical Sulfuric Acid Source, *Chem. & Met. Eng.*, **44**, 376 (1937); WOISIN, Manufacture of Sulfuric Acid from H_2S in Coke-oven Gas by Moist Catalysis, *Chem. & Met. Eng.*, **43**, 301 (1936).

[2] SPANGLER and TITLESTAD, Modern Pickle Recovery, *Wire and Wire Products*, October, 1938; ANON., Sulfur Dioxide Recovery, *Chem. & Met. Eng.*, **42**, 608 (1935); GEHM, Recovery of Chemicals from Pickling Liquor and Copperas Waste, *Ind. Eng. Chem.*, **34**, 382 (1942).

$$4FeSO_4 + C \rightarrow 2Fe_2O_3 + 4SO_2 + CO_2$$
$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

As shown in the flow sheet, the free H_2SO_4 of the original liquor is neutralized with Fe_2O_3 to produce a relatively dry sulfate of iron. The iron sulfide is added to reduce the amount of coal otherwise required and to supply additional SO_2 needed for this particular plant which now makes 250 tons of contact acid per day.

The oil refineries get considerable tonnage of a dirty "sludge acid" from the sulfuric acid purification of petroleum products. The old process of adding water, separating, and concentrating the dilute sulfuric acid never yielded a good acid recovery, and it was troublesome to operate. A number of plants are now operating on the *Chemico*[1] *sludge conversion process* wherein the acid sludge plus red-hot coke is heated to about 550°F. resulting in more solid coke, water vapor, some hydrocarbons, and sulfur dioxide (15 to 25 per cent SO_2 by volume). After being cooled and purified, the sulfur dioxide is converted to sulfuric acid by the contact process (see Fig 3).

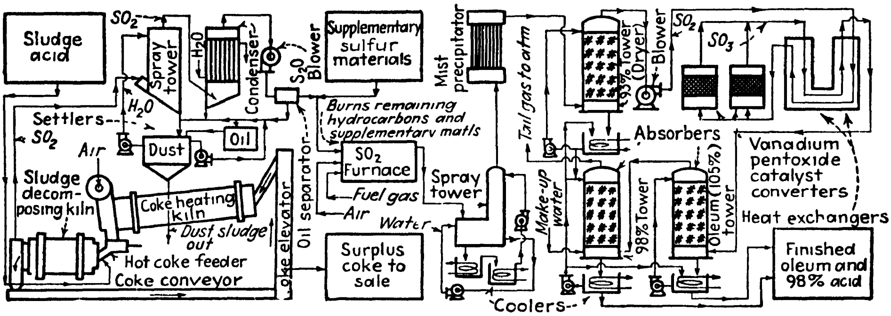

FIG. 3.—Sulfuric acid from sludge acid.

Nearly a third of the sulfuric acid manufactured obtains its sulfur dioxide either from waste smelter gases or from the direct roasting of either domestic or imported pyrite.

SULFURIC ACID

It seems hard to believe that a very active chemical, such as sulfuric acid, is at the same time one of the most widely used and most important of technical products. It is of such paramount significance that the remark has frequently been made that the per capita use of sulfuric acid is an index of the technical development of a nation. Sulfuric acid is the agent for sulfate formation and for sulfonation but is used more frequently by virtue of being a rather strong and economically priced inorganic acid. It enters into countless industries, though infrequently appearing in the finished material. It thus aids in the manufacture of leather and tin plate, in the purification of petroleum, and in the dyeing of fabrics.

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[1] SPANGLER, Modified Acid Recovery Process Treats Troublesome Acid Sludges, *Chem. & Met. Eng.*, **44**, 368 (1937); ANON., Sulfuric Acid from Refinery Sludge, *Chem. & Met. Eng.*, **48**, No. 5, 144 (1941). The latter presents an excellent pictured flow sheet, depicting particularly the purification of the sulfur dioxide that is formed.

Historical.[1]—The origin of the first sulfuric acid is unknown, but it is mentioned as far back as the tenth century. The preparation is first described by Valentinus in the fifteenth century. He tells of its preparation by burning saltpeter with sulfur. In 1746, Dr. Roebuck of Birmingham, England, introduced the lead chamber. His process consisted of placing a mixture of brimstone and saltpeter in iron carts and rolling them into the chamber where the reactions took place. In 1774, steam was first used in the chambers. Early in the nineteenth century, the continuous method replaced batch operation. Another notable improvement in the process was the invention of the Gay-Lussac tower for the recovery of nitrogen oxides in 1827, which, however, was not applied until the invention of the Glover tower in 1859. Meanwhile the art of lead burning had been developed in 1838. The Glover tower furnished a means of denitrating the nitrous acid from the Gay-Lussac tower without diluting it with too much water; it complemented the use of the Gay-Lussac tower. Since that time both towers have been standard equipment on all lead-chamber processes. Many improvements, some of an economic nature, have been devised in recent years to help the chamber process to compete with the newer contact process, but this seems to be a losing contest except where weak or chamber acid can be consumed *directly*, as in superphosphate manufacture.

The contact process was first discovered in 1831 by Phillips, an Englishman, whose patent included the essential features of the modern contact process, namely, the passing of a mixture of sulfur dioxide over a catalyst followed by absorption of the sulfur trioxide in water. Phillips's invention was not a commercial success for more than 40 years, probably owing to (1) the lack of demand for fuming acids, (2) inadequate knowledge of catalytic gas reactions, and (3) the slow progress of chemical technology. The early years of the dye industry afforded a rising demand for fuming acids for the manufacture of alizarin and other organic coloring matters.

At first, fuming sulfuric acid was made by decomposing chamber acid by means of heat.

$$H_2SO_4 \xrightarrow{\Delta} H_2O + SO_2 + \tfrac{1}{2}O_2$$

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[1] Fairlie, "Manufacture of Sulfuric Acid," Reinhold Publishing Corporation, New York, 1936. This is the standard reference book on sulfuric acid and should be freely consulted. Many references and sketches are included.

The sulfur dioxide and oxygen were dried and then passed over a catalyst and absorbed in the chamber acid. This method was used until 1881, when sulfur trioxide was made by passing sulfur dioxide and a theoretical amount of air over a mixture of platinized asbestos. In 1889 it was demonstrated that *excess* of oxygen in the gaseous mixture was advantageous. In recent years the contact process has been improved in all its details until it is now one of industry's low-cost, almost wholly automatic processes (see Fig. 9).

Properties of Sulfuric Acid.—Sulfuric acid is a strong dibasic acid. In addition, it is also an oxidizing and a dehydrating agent particularly toward organic compounds. The dehydrating action is important in absorbing water formed in such unit processes as nitration, esterification. and sulfonation, thus ensuring high yields. Solutions of sulfuric acid may be concentrated economically to about 93 per cent by weight of H_2SO_4. Stronger sulfuric acids may be made by dissolving sulfur trioxide in this concentrated acid. Sulfur trioxide forms many hydrates that have fairly definite melting points, as shown in Table 2. The irregularities in the relation between strengths of the sulfuric acids and the corresponding specific gravities and freezing points are due to these hydrates.

TABLE 2.—HYDRATES OF SULFURIC ACID[a] AND SULFUR TRIOXIDE

	Formula	Melting point, °C.	Specific gravity
Pyrosulfuric acid	$H_2S_2O_7$	35	$1.9^{20°}$
Monohydrate	H_2SO_4	10.49	$1.834^{18/4°}$
Double hydrate	$H_2SO_4 \cdot H_2O$	8.62	$1.842^{15/4°}$
Triple hydrate	$H_2SO_4 \cdot 2H_2O$	−38.9	$1.650^{9/4°}$
Quintuple hydrate	$H_2SO_4 \cdot 4H_2O$	−25	

[a] PERRY, *op. cit.*, p. 362; FAIRLIE, "Manufacture of Sulfuric Acid," p. 48, Reinhold Publishing Corporation, New York, 1936.

Sulfuric acid is widely sold in the form of various solutions of H_2SO_4 in water or of SO_3 in H_2SO_4. These latter are called *oleums* and are marketed on the basis of the percentage of SO_3 present; 20 per cent oleum means that in 100 lb. there are 20 lb. of SO_3 and 80 lb. of H_2SO_4. This 20 per cent oleum if diluted with water to make monohydrate, H_2SO_4, would furnish 104.5 lb. For convenience, now grown into an established custom, the ordinary solutions of sulfuric acid and water are sold according to their gravity, or their Baumé degree. Table 3 illustrates the sulfuric acids of commerce. The usual temperature to which specific gravity or Baumé (Bé.) is referred is 60°F. for sulfuric acids. The specific gravity of sulfuric acid increases gradually to 1.844 at 60°F. for 97 per cent sulfuric acid, after which it decreases to 1.835 at 60°F. for

100 per cent acid. Consequently in this upper range, *i.e.*, above 95 per cent, the strengths should be determined by other means, such as electrical conductivities, titrations, or heat rises. For some of the medium-range oleums, however, specific gravity is again helpful.

TABLE 3.—COMMERCIAL STRENGTHS OF SULFURIC ACID (60°F.)[a]

	Degree Bé., 60°F. or 15.6°C.	Specific gravity, 60°F. or 15.6°C.	Sulfuric acid, per cent
Battery acid	29.0	1.250	33.4
Chamber acid, fertilizer acid, 50° acid	50	1.526	62.18
Glover or tower acid, 60° acid	60	1.706	77.67
Oil of vitriol (O.V.), concentrated acid, 66° acid	66	1.835	93.19
98° acid	66.2	1.841	98.0
Monohydrate, H_2SO_4	65.98	1.835	100.0
20 per cent fuming, 20 per cent oleum, 104.5° acid		1.927	104.49, 20 per cent free SO_3
40 per cent oleum, 109° acid		1.965	109.0, 40 per cent free SO_3
65 per cent oleum		1.990	114.6, 65 per cent free SO_3

[a] PERRY, *op. cit.*, pp. 428–429; 94–95. There are minor differences between different sulfuric acid tables.

The normal strengths of commercial oleums are usually 20, 40, 60, and 65 per cent of free sulfur trioxide, the 20 and 60 being the most common. The 20 per cent oleum has a melting point of about −10°C., and the 65 per cent oleum has a melting point of 0°C. It is interesting to note that the melting point of 45 per cent oleum is about 35°C. This fact accounts for the relatively small shipments of the 45 per cent oleum; the 40 or 45 per cent oleum may be made and mixed with nitric acid with consequent reduction in the melting point.

Uses of Sulfuric Acid.—The most important use on the tonnage basis is for the manufacture of superphosphate fertilizer which employs chamber acid of 50 to 55°Bé. In the petroleum industry sulfuric acid is employed as a catalyst for the polymerization of olefins, as a reactant in the making of additional compounds from olefins, and as a refining agent for many petroleum products. In organic chemical industry it is a sulfonating agent; an ingredient of mixed acid for the manufacture of such explosives as cellulose nitrate, glyceryl nitrate, picric acid, and T.N.T.; as a catalyst for the manufacture of organic esters such as ethyl acetate, methyl salicylate, ethyl benzoate, and many others; as a reactant in the manufacture of chloro-acetic acid, citric acid, creosote, quinidine, hydrocyanic acid, tartaric acid, and adipic acid; and as a hydrolysis reagent for carbohydrates and starch. In the inorganic industries, besides its use in analytical work and as an acidifying and neutralizing agent for alkalies, it is employed as a concentrating agent for hydrogen peroxide and weak nitric acid, and in the making of salt cake and hydrochloric acid, phosphoric acid, potassium bichromate, aluminum sulfate, iron sulfate, and other sulfates such as potassium, ammonium, barium, magnesium, manganese, copper, zinc, and mercury. In the metallurgical industries it is used as a cleansing agent for brass, bronze, copper, iron, silver, and steel; as a pickling agent for iron and steel; as a desilvering agent for copper; and as a process material in the metallurgy of cobalt, copper, gold, iron, magnesium, nickel, platinum, and silver. It is applied to form the electrolyte in the electrolytic process in metallurgy and in electroplating, as an electrolyte in storage batteries, and in the electrolytic production of many organic chemicals.

In the textile industries sulfuric acid serves to make white sour in bleaching cotton goods, in the sulfation of castor oil leading to Turkey-red oil, in the carbonizing of woolens, dyeing, and mercerizing processes, and as an acid dyeing assistant. It is employed in the manufacture of many organic chemicals, both aromatic, aliphatic, and heterocyclic.

Miscellaneous uses include the field of glue, gelatine, and leather, as a recovery agent for fatty acids in the manufacture of soap, as a reactant in rubber reclamation, in lithographic processes, for engraving, as a paper parchmentizing agent, in the manufacture of fungicides, in the making of candles, and in the fermenting industry to produce a favorable pH.

TABLE 4.—SULFURIC ACID CONSUMED IN THE UNITED STATES BY INDUSTRIES (AS 50°Bé.)[a]
(In short tons)

	1940	1941
Fertilizer	2,260,000	2,500,000
Petroleum refining	1,260,000	1,400,000
Chemicals	1,120,000	1,790,000
Coal products	900,000	940,000
Iron and steel	1,200,000	1,450,000
Other metallurgical	640,000	800,000
Paints and pigments	580,000	700,000
Explosives	170,000	190,000
Rayon and cellulose film	470,000	555,000
Textiles	125,000	165,000
Miscellaneous	460,000	550,000
Totals	9,185,000	11,040,000

[a] "Minerals Yearbook," 1941, U.S. Bureau of Mines. It is estimated by *Chem. & Met. Eng.*, **51**, No. 2, 112 (1944), that the production in 1943 was 13,930,000 tons.

Manufacture.—There have long been two main procedures for the making of sulfuric acid: the chamber process and the contact process. Both are based on sulfur dioxide, both are catalytic, both use air as the source of oxygen for making the sulfur trioxide, and both have been operated on a large scale for many years.[1] The chamber process produces directly a weaker acid of from 50 to 55°Bé., and up to 66°Bé. acid by concentration. On the other hand, the contact process produces 98 and 100 per cent acids and the various oleums. Much 66°Bé. acid results by dilution. Unless the weak chamber acids can be consumed directly, as for producing superphosphate, the present economics point to a production of more and more oil of vitriol (93.19 per cent H_2SO_4) by the contact process rather than by concentration of chamber acid.

MANUFACTURE BY THE CHAMBER PROCESS

A typical flow sheet for the chamber process is presented in Fig. 4. The process starts when either the sulfur or pyrite is burned and the hot gases are conducted through a combustion chamber which also may collect some dust. Sufficient oxides of nitrogen, NO and NO_2, are introduced into the hot mixture of air and sulfur dioxide from the burner. This may be done either by the use of niter pots or by an ammonia oxidation unit. The hot gaseous mixture passes up the Glover tower where it is met by the downward flow of the diluted Gay-Lussac acid or the nitrous vitriol. In the Glover tower about 10 per cent of the sulfuric acid is produced, the so-called *tower acid.* If an ammonia oxidation unit supplies the nitrogen oxide, this is preferably entered into the gas stream, as shown by Fig. 4, after the gas has been cooled by its passage up the Glover tower. The cooled gases are blown to the chambers where most of the acid is made and condensed. Finally, the unreacted gases pass to the Gay-Lussac tower for the absorption of the oxides of nitrogen in the strong Glover acid, producing the Gay-Lussac acid or the nitrous vitriol.

Reactions.—The conversion of the sulfur dioxide to sulfuric acid involves many fairly complex chemical changes. The over-all reaction is[2]

$$SO_2 + \tfrac{1}{2}O_2 + H_2O(l) \rightarrow H_2SO_4; \qquad \Delta H = -54{,}500 \text{ cal.}$$

The detailed reactions may be formulated (Lunge-Berl):

In the gaseous phase, homogenous:

$$2NO + O_2 \rightarrow 2NO_2 \tag{1}$$

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[1] A chart of the distribution of sulfuric acid plants in the United States, as of a few years ago, is given in Perry, *op. cit.*, p. 2837; *cf.* "Rogers' Manual of Industrial Chemistry" 6th ed., p. 245, D. Van Nostrand Company, Inc., New York, 1942.

[2] Fairlie, *op. cit.* p. 37; Berl, Studies of the Lead Chamber Process, ***Trans. Am. Inst. Chem. Engrs.***, **31**, 193 (1935).

On the gas-liquid interface, heterogenous on wetted walls:

$$SO_2 + H_2O \rightarrow H_2SO_3 \qquad (2)$$

$$H_2SO_3 + NO_2 \rightarrow H_2SO_3{\cdot}NO_2 \text{ (violet acid or nitrosulfuric acid)} \qquad (3)$$

$$2(H_2SO_3{\cdot}NO_2) + \tfrac{1}{2}O_2 \text{ (from } NO_2 \rightarrow NO + \tfrac{1}{2}O_2)$$
$$\rightarrow H_2O + 2(HSO_3{\cdot}NO_2) \text{ (nitrosyl sulfuric acid or nitro acid sulfite or chamber crystals)} \qquad (4a)$$

$$2(HSO_3{\cdot}NO_2) + SO_2 + 2H_2O \rightleftarrows 2(H_2SO_3{\cdot}NO_2) + H_2SO_4 \qquad (5a)$$

In the liquid phase, homogenous:

$$H_2SO_3{\cdot}NO_2 \rightleftarrows H_2SO_4 + NO \qquad (4b)$$

$$2(HSO_3{\cdot}NO_2) + H_2O \rightleftarrows 2H_2SO_4 + NO + NO_2 \qquad (5b)$$

$$HSO_3{\cdot}NO_2 + HNO_3 \rightleftarrows 2NO_2 + H_2SO_4 \qquad (5c)$$

($HSO_3{\cdot}NO_2$ is sometimes written SO_5NH, and $H_2SO_3{\cdot}NO_2$ as $H_2SO_4{\cdot}NO$)

The important characteristics of the chamber process are the circulation of the catalytic oxides of nitrogen and the equipment needed for this, but the heat of reaction must be dissipated to secure the desired favorable equilibriums.

Unit Operations, Unit Processes, and Energy Changes.—The flow chart (Fig. 4) may be broken down into the following coordinated sequence of *unit operations* (Op.) and *unit processes* (Pr.):

Transportation of sulfur or sulfides to plant (Op.).

Melting of sulfur (Op.).

Burning of sulfur or sulfide (Pr.).

Recovery of heat from hot sulfur dioxide gas (Op.).

Purification of sulfur dioxide gas (Op.).

Mixing of sulfur dioxide gas with the nitrogen oxides catalyst in Glover tower (Pr. and Op.).

Oxidation of sulfur dioxide to sulfur trioxide (see Reactions) (Pr.).

Hydration of sulfur trioxide to sulfuric acid in Glover tower and chambers (Pr.).

Settling of sulfuric acid mist and dissipation of heat of reactions (Op.).

Absorption of nitrogen oxides from residual gas, forming nitrous-vitriol in Gay-Lussac tower (Pr.).

Pumping of acids over towers and through coolers (Op.).

Blowing of gases through system (Op.).

Oxidizing of ammonia to nitrogen oxide, NO, for catalyst make-up (Pr.).

The energy changes necessary to carry the chamber process into effect involve not only the dissipation of the energy set free by the over-all reaction but the supplying of the small amount of power shown on the flow sheet (Fig. 4) for the moving of the gases and liquids. In a few of the newer plants part of the over-all chemical energy is turned into useful work through by-product boilers following the sulfur dioxide furnace.

In some detail, these unit sequences may be elaborated in connection with the chamber process flow sheet, classified largely by the typical equipment commercially employed. Corrosion in such equipment can be avoided by the proper choice of the materials for construction.[1]

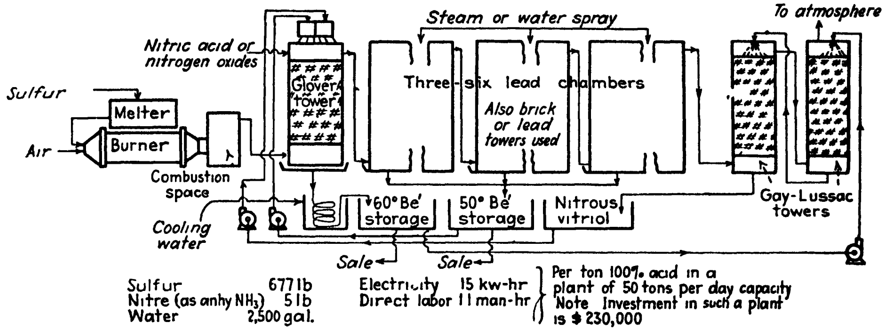

FIG. 4.—Sulfuric acid manufacture by the chamber process.

Burners and Furnaces.[2]—The type of burner for producing the sulfur dioxide is determined by the raw material available for the process. The chief material is sulfur or brimstone, although pyrite, FeS_2, is used very extensively, as well as pyrrhotite, Fe_7S_8. Other processes for obtaining sulfur dioxide have been devised and are now in operation, producing it as a by-product in the refining of zinc and copper from sulfide ores, from the pyrite from coal waste, from waste ferrous sulfate liquors (flow sheet of Fig. 2), and from hydrogen sulfide gases from natural and refinery gases and other sources.

If sulfur itself is burned, one type of burner that has been used much in the past consists merely of a horizontal revolving steel cylinder, surmounted by a pan for melting the sulfur before introduction into the cylinder. This is shown in Fig. 4 and is called the *Glens Falls burner*. The more modern procedure is to melt the sulfur with steam in pipes and pump the liquid into a furnace where it is atomized and burned to sulfur dioxide. This is depicted in Fig. 9 and was introduced by the Chemical Construction Co.

If coarse pyrite is available, lump burners or roasters are employed. The lump burners are much like deep-bed coal grates and are frequently built in batteries of 24 burners, constructed of brick and faced with cast-iron plates. The grate bars are supported on bearings to facilitate shaking. Cinders are removed from openings in the cast-iron front, and charging is done similarly.

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[1] *Cf.* PERRY, *op. cit.*, pp. 2100–2101, where tables of corrosion-resistant materials are presented.

[2] BUTCHER, Pyrites Roasting and Sulphur Burning, *Chem. Age*, 41, 411 (1939).

Much fine sulfide of copper or zinc or iron is burned. Here a multiple hearth is employed with mechanical stirring and moving of the "fines" to secure efficient oxidation. The roasters generally consist of a central rotating shaft with arms extended from the center over each hearth. The fines are fed into the top of the roaster and dropped upon the top hearth where burning of the ore is started. The partly burned ore is caused to drop downward to the lower hearth by the rotating arm. This is continued to the bottom hearth where the cinder is removed. The gases pass out the top to be used.[1] Several of the newer plants are burning very fine pyrite or other sulfide ore by blowing it into the furnace usually in connection with by-product boilers.

In general, the production of sulfur dioxide for the contact process is the same for the chamber process. The types of furnace and raw materials do not change, nor the furnace that would be adapted to a given raw material. The percentages of sulfur dioxide and oxygen in the gas issuing from the burner are very carefully controlled and the desired concentrations varied with the process used. For platinum catalysts 10 per cent sulfur dioxide is desired while vanadium catalysts operate best with gas containing from 7 to 8 per cent sulfur dioxide. It should be noted that the percentage of oxygen decreases as that of the sulfur dioxide increases and that where gases of lower percentage of sulfur dioxide are processed larger volumes of gas must be handled.

Dust Removal.—When sulfide ores are the source of the sulfur dioxide, dust removal becomes important. Many methods[2] have been tried for removing dust from the gases, usually by reducing the velocity of the gas stream in large chambers without baffle walls. These are built in duplicate so that while one is being cleaned the other is in service. Centrifugal cyclone dust catchers are also used, wherein the particles are separated from the gas stream by impingement on the walls of the apparatus. A third type of dust collector is the Cottrell or electrical precipitator. In this the gases are allowed to pass through a direct-current, high-voltage (30,000 to 80,000 volts) electrical field, where a silent discharge of negative polarity ionizes the gas, causing the dust particles to become electrically charged and, therefore, to be precipitated on the collecting electrode. The dust falls to hoppers from which it is removed. The gases, after going through the dust collectors and by-product boilers, pass to where the nitrous oxides are introduced.

Introduction of the Oxides of Nitrogen.[3]—The introduction of the "oxides of nitrogen" may be done in one of the following ways: (1) by the heating of sodium nitrate and 60°Bé. sulfuric acid in cast-iron pots inside the sulfur dioxide gas flue or by heating sodium nitrate and the acid in a furnace outside the flue—the "potting" procedure, (2) by feeding mixed nitric and sulfuric acid into the top of a Glover tower or at times liquid nitric acid alone, (3) by feeding a solution of sodium nitrate and sulfuric acid into a small tower operated in parallel or in series with the Glover tower, (4) by spraying a solution of sodium nitrate into the first chamber, or (5) by the oxidation of ammonia and the conduction of the oxides either into the Glover tower or the first chamber.

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[1] FAIRLIE, *op. cit.*, pp. 98–107.

[2] FAIRLIE, *op. cit.*, pp. 134–142; PERRY, *op. cit.*, chambers, pp. 1855 and 1862, cyclones, p. 1863, electrical precipitation, p. 1867.

[3] FAIRLIE, *op. cit.*, Chap. 7, p. 143.

The success of the ammonia oxidation and the cheap synthetic ammonia available have rendered the use of sodium nitrate obsolete. The ammonia is mixed with air and passed through a platinum gauze catalyst maintained at 950 to 1000°C. by the heat of reaction. Hot nitrogen oxide is used to preheat the incoming air and to maintain the catalyst at red heat. This gives a relatively inexpensive method for producing nitrogen oxide. The advantages of this method are (1) no sulfuric acid needed, (2) low cost of raw materials, (3) high purity of the gases produced (no hydrochloric acid present to injure the lead chamber), (4) a constant and continuous supply of the oxide, (5) lower labor costs because of simplicity of operation, (6) equipment that is longer lasting and lower in maintenance, and (7) no by-product to dispose of. When nitrogen oxide from ammonia is used, it is introduced into the SO_2 gas after the latter has passed up the Glover tower. The economy is shown by the fact that nitrogen oxide cost on a yearly basis is about half of that of sodium nitrate.

Glover Towers.—The functions of the Glover tower are

1. The denitration of nitrous vitriol (Gay-Lussac acid). This is effected by reducing the solubility of nitrogen oxides by dilution and heat, aided by the passage of gases.
2. The conversion of the make-up nitric acid to nitrous acid and to nitrogen oxides (omitted when NO from NH_3 is introduced).
3. The concentration of that part of the chamber acid which is added to dilute the 60° Bé. (77.7 per cent) Gay-Lussac acid to 57°Bé. (72.8 per cent) at the top of the tower.
4. The cooling of the furnace gases.
5. The production of acid from about 10 per cent of the sulfur dioxide. This takes place in the upper part of the tower.
6. The cleaning of the furnace gases.
7. The production of steam for the chambers.
8. The production of partly concentrated acid (60°Bé. or 77.7 per cent or slightly stronger) suitable for passing down the Gay-Lussac tower.

The Glover towers[1] are either all-masonry towers built from acidproof bricks with acidproof cement or of lead supported by an outside steel frame. At the bottom of the tower there is a brick flue inlet for the gases, and at the top there is a distributing device for the Gay-Lussac acid which is diluted to 57°Bé. or 72.8 per cent and caused to flow down the tower. The interior of the tower is packed[1] with hard-burned brick or tile made in a number of different designs. The cooled gases pass out near the top of the tower and are piped to the first chamber. The hot (140 to 160°C.) Glover or "tower" acid is collected at the bottom of the tower in a lead pan and passed through an acid cooler. Part is used over in the Gay-Lussac tower and the rest concentrated for consumption or sale. The amount of acid necessary to circulate over the Gay-Lussac tower and then to the Glover tower is from three to four times the daily production of acid, based on 60°Bé.

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[1] FAIRLIE, *op. cit.*, Chap. 8, p. 159. Heat balance, p. 170.

The sulfurous gases enter the tower between 425 and 600°C. About 10 per cent of the sulfur dioxide is oxidized in the Glover tower. The gaseous mixture of SO_2, SO_3, N_2, O_2, NO, NO_2, N_2O_3, and steam leaves a Glover tower at a temperature of from 70 to 110°C. and is sucked to the chamber by means of a fan.

Chambers.—It is in the chambers that the greatest proportion of sulfur dioxide is oxidized to sulfur trioxide and hydrated to sulfuric acid. The chambers consist of a large steel framework with an interior of lead sheets which are "burned" or welded together with lead. These lead chambers are generally built about 10 ft. above the ground so that leaks in the bottoms may be easily detected and cooling may be facilitated. The reactions in the chamber generate much heat which must be removed continuously if the rate of sulfuric acid production is to be maintained. Under the ordinary condition of construction for chambers, this heat is dissipated slowly. Also some of the reactions proceed at a low rate. Thus, ordinarily, considerable space is needed in the chambers amounting to from 7.5 to 10 cu. ft. per lb. of sulfur burned per 24 hr. This can be much reduced by special cooling and mixing devices. The chambers may be enclosed in a building that is usually air-cooled. With good operation the average chamber set lasts over 20 years. Although, formerly, steam was introduced into the chambers, with the present excellent atomizing equipment water is used almost universally.

Gay-Lussac Tower and Recovery of Nitrogen Oxides.—The function of the Gay-Lussac tower[2] is to recover the nitrogen oxides (catalyst) from spent gases. This is accomplished by washing these gases which should not be warmer than 60°C. with cold strong (60°Bé.) Glover acid in packed towers. There results the nitrous vitriol or Gay-Lussac acid containing 1 to 2 per cent of oxides of nitrogen, calculated as N_2O_3. The modern

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[1] PERRY, *op. cit.*, pp. 1198–1206. Various types of packing are illustrated and tabulated.

[2] FAIRLIE, *op. cit.*, Chap. 10, p. 223.

Gay-Lussac towers are constructed of masonry with acidproof cement. They are much taller and narrower and have thinner walls than the Glover tower. In the bottom of the tower is a pan of lead to collect the nitrous vitriol from which it is pumped over the Glover tower. The packing of the Gay-Lussac tower, like that of the Glover tower, is made of special shapes of hard-burned ceramic material.

Concentration of the Acid.—The acid issuing from the Glover tower is usually between 60 and 61°Bé. in strength, and from the chambers, 50 to 55°Bé. For many purposes it is desired to concentrate these acids. Much process sulfuric acid must be reconcentrated after use. This is true of denitrated spent acids from making nitro compounds or nitrate esters, and of the sulfuric acid used to manufacture strong (95 per cent) nitric acid. These spent acids illustrate the important dehydrating action of strong sulfuric acid. Other acids that must be recovered and reconcentrated are sludge acids from petroleum purification and the sulfuric acid from the viscose rayon coagulation bath.

Sulfuric acid may be concentrated to around 66°Bé. by heat. Any further fortification usually is done by the addition of oleum or sulfur trioxide in a contact plant. One of the older but now obsolete types of concentrators consisted of basins of cast iron or silica in cascade formation over a furnace. The present equipment for concentrating dilute sulfuric acids employs either hot combustion gases in direct contact with the acid being concentrated or high-pressure steam heating through an interface with the acid under vacuum. Relatively high temperatures are required, owing to the low vapor pressures[1] of the sulfuric acid as it approaches 66°Bé. or 93.2 per cent. If hot combustion gases are used, some sulfuric acid is entrained as a mist which would be a nuisance if allowed to escape. This is caught in a coke-packed box or by a Cottrell electrostatic precipitator.[2] The precipitated acid is returned to the concentrator. Any sulfur dioxide formed by reduction of sulfuric acid by organic matter present in the spent acid escapes through the precipitator to the atmosphere.

The hot gas concentrator is exemplified by the Chemico[3] drum-type concentrator which is shown in Fig. 5. The drum concentrator acts by surface evaporation of the water from the sulfuric acid, heated by blowing the hot combustion gases countercurrent over and through three baths of the acid. The long horizontal drum is divided into four compartments as can be seen from Fig. 5. The first compartment is of steel lined with firebrick and is the combustion space for oil or fuel gas furnishing hot combustion gases at 1100°F. These hot gases are led through heat- and acid-resistant iron pipes from one compartment to the other, being released slightly below the acid surface. The temperature of the gases entering the front concentrating compartment is around 1100°F., and

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[1] Perry, *op. cit.*, p. 398; Zeisberg, Thermal Considerations in Sulfuric Acid Concentrations, *Trans. Am. Inst. Chem. Engrs.*, **14**, 1–11 (1922); Rogers, *op. cit.*, pp. 241, 302 where tables and curves of boiling points are given. For recent studies, see Parrish, Modern Improvements in the Design of Plant for the Concentration of Sulfuric Acid, *Trans. Inst. Chem. Engrs.*, (London) **19**, 1 (1941); Kalous, Improvements in Concentrating Sulfuric Acid, *Ind. Eng. Chem.*, **35**, 387 (1943).

[2] Perry, *op. cit.*, pp. 1867–1878.

[3] Chemical Construction Corp., New York.

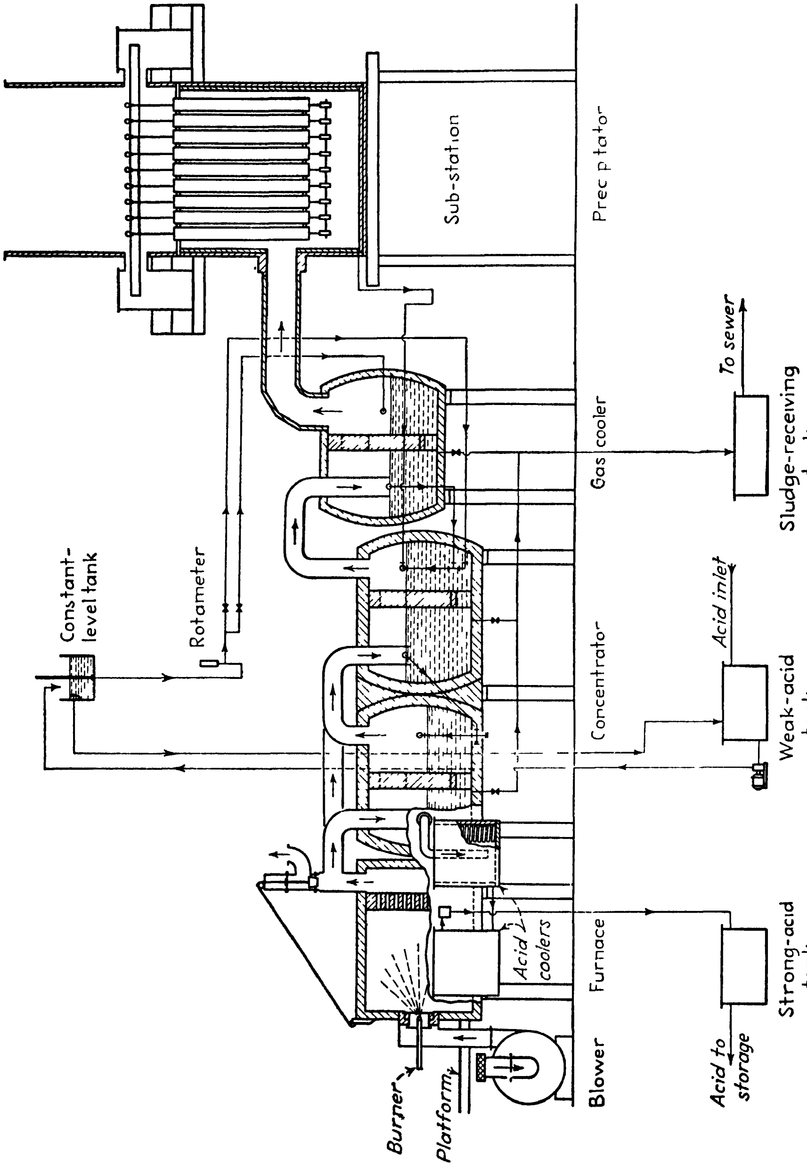

FIG. 5.—"Chemico" sulfuric acid concentrator, drum type. (*Courtesy of Chemical Construction Corporation.*)

around 450°F. when leaving to enter the middle compartment. Through this middle compartment is also bubbled part of the hot combustion gases. The temperature when leaving the rear compartment and entering the duct to the Cottrell precipitator is around 200 to 250°F., when concentrating the acid to 66°Bé. This represents excellent thermal efficiency for this kind of concentration. The hot gases also burn out any dangerous impurities that may be in a spent acid being concentrated. Hence such concentrators are being extensively employed in the concentration of spent nitrating acids from munition works. Normally the acid to be concentrated flows continuously and without interruption from rear to front where it is cooled and discharged around 92 to 95 per cent sulfuric acid. However, if sludge acid from petroleum purification is being handled, the flow of acid from rear to front compartment is passed through an intermediate storage tank where a skimmer removes most of the nonvolatile carbonaceous impurities. The front and rear concentrating compartments of the steel drum are lined with lead and acidproof masonry. The repairs are remarkably low. Inside each drum of Fig. 5 is shown a vertical baffle to minimize the mechanical carry-over of acid mist and to lessen the burden on the Cottrell precipitator.

A tower[1] concentrator has also been used wherein the weak acid flows down against the rising hot gases from a combustion chamber. No new tower concentrators have been built for many years.

The steam-heated vacuum concentrators are exemplified by the Simonson-Mantius vacuum concentrator and the Chemico flash film concentrator. The former is a batch type and is presented in Fig. 6. It employs, particularly at the end of a batch, a *high vacuum* (29.8 in.) to reduce the boiling point of the sulfuric acid. It is a cleanly operating and efficient equipment. Dr. Otto Mantius[2] states, "Charges for maintenance and repairs for larger units will be about 20 cents per ton of acid produced, for smaller plants about 30 cents." To get 93 per cent acid from 78 per cent, 1,400 lb. of 100-lb. steam are required, basis 1 ton of 100 per cent acid. This 1,400 lb. of steam includes both the heating steam and that required for vacuum maintenance; this however does not include the steam required for initial heating of weak acid to boiling point. The concentrator itself is a steel shell lined with lead and acidproof brick. The central brick supporting column is not necessary for concentrators of 12 ft. and smaller diameter. The inward protruding closed end heating tubes are made of Duriron or other sulfuric-acid-resisting alloy.

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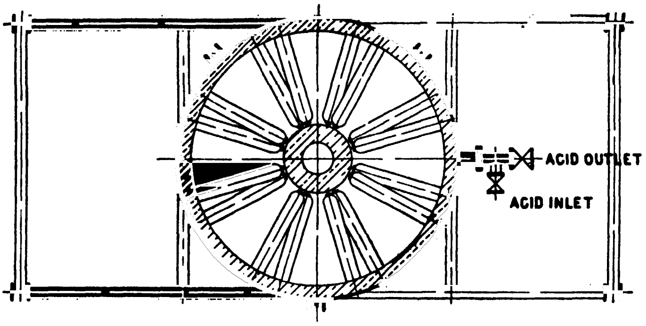
[1] Such tower concentrators have been built by Kalbperry Corp. and the Chemical Construction Corp. See FAIRLIE, *op. cit.*, pp. 319–324; WELLS and FOGG, The Manufacture of Sulfuric Acid, pp. 138–140, *Bull.* 184, U.S. Bureau of Mines, 1920.

[2] *Private communication; cf.* also circulars of National Lead Co. and pp. 301–308, 241 of Rogers, *op. cit.*



SECTIONAL PLAN

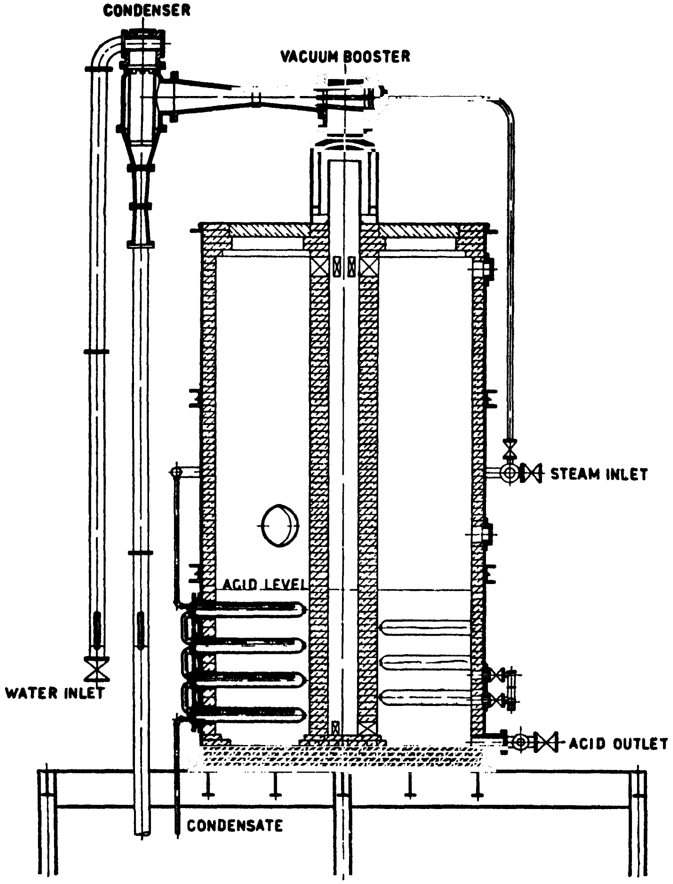


Fig. 6.—Simonson-Mantius vacuum concentrator for sulfuric acid. (*Courtesy of National Lead Company.*)

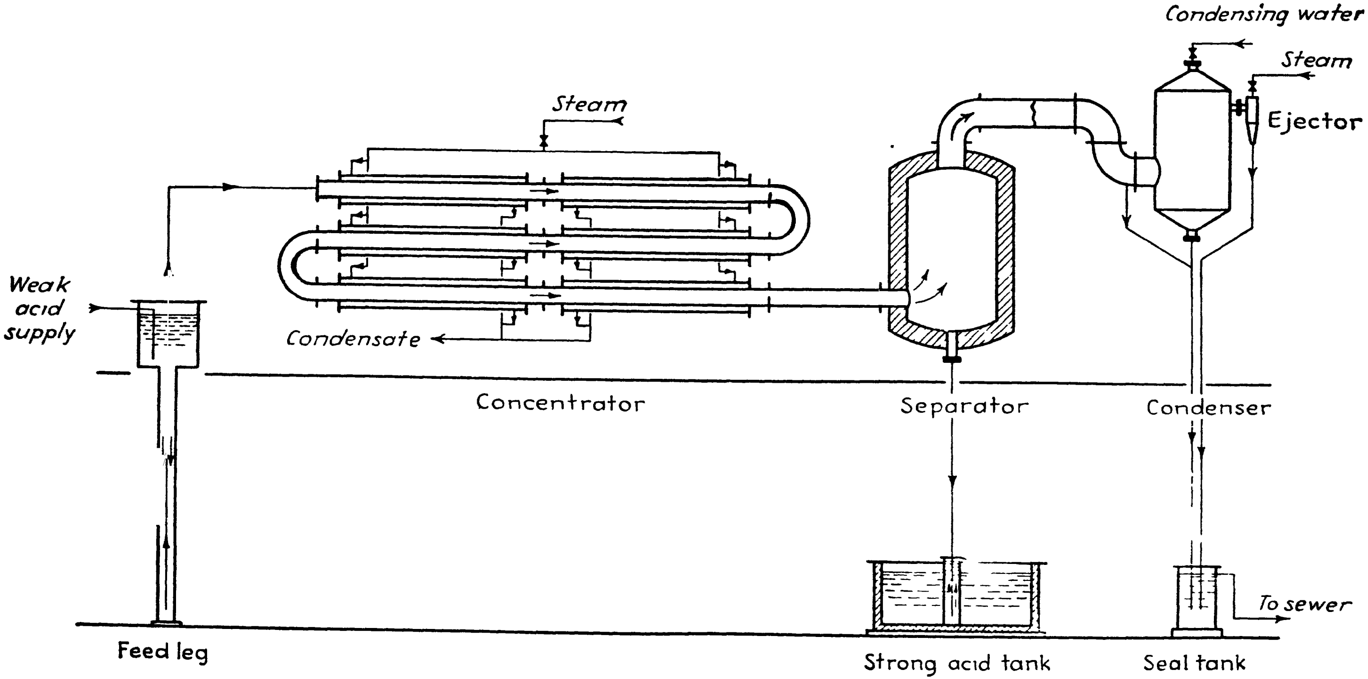


Fig. 7.—"Chemico" sulfuric acid concentrating process, flash-film vacuum type. (*Courtesy of Chemical Construction Corporation.*)

The Chemico flash film concentrator as shown by Fig. 7 is a continuous apparatus with the weak acid to be concentrated passing down through a series of connected return bends of high silicon acidproof pipe, jacketed for steam. It operates usually under vacuum produced by a steam ejector and a barometric leg. Because of the rapid acid flow in films, an efficient heat transfer is attained. This type of concentrator is also used to distill 95 per cent HNO_3 from tower nitric acid as weak as 50 per cent, using strong sulfuric acid as the dehydrating agent. The weakened sulfuric acid can then be reconcentrated in another such unit.

Improvements in the Chamber Process.—Because of the large volume of acid made by the chamber process, there have been many new designs introduced to better the economics of this process. One of the first of these was the Pratt procedure which obtained popularity between 1890 and 1910. It differed from the ordinary plants by having the first chamber much larger than the others and by placing between the first and second chambers a tower known as the *converter*. This was a packed tower, about 25 ft. in height, which provided intimate mixing and, therefore, produced a large amount of acid. The gases issuing from the top of the tower were divided and part of them fed back into the largest chamber, the other part being sent on to the smaller chambers.

In 1913 in England there were erected chambers in the shape of truncated cones with provision for water cooling on the outside. These were invented by Mills and Packard.[1] Such chambers reduce the space per pound of brimstone burned per day from 8 to about 3 cu. ft. Redesigned plants of this type may be constructed so compactly that chambers for a 100-ton plant may be erected on 100 sq. ft. of ground. Recently at Tampa, Fla., a 300-ton (60°Bé.) per day plant has been put into operation.[2] This is illustrated by Fig. 8. It needs only 2.75 cu. ft. of chamber space per pound of sulfur burned per day.

Another plant for the reduction of space is the Gaillard-Parrish acid-cooled chamber. This consists of a steel-framed cylindrical lead chamber which has at the top a "turbodispenser" that cools the chamber walls from the inside by spraying them with a shower by a finely divided precooled chamber acid. These towers are usually 50 ft. or more tall and may handle 500 to 2,000 tons of chamber acid per hour. Here again only about 3 cu. ft. of chamber space is needed per pound of brimstone burned per day.

An interesting plant has been installed by the Anaconda Copper Company at Anaconda, Mont. This consists of the usual Glover and

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[1] FAIRLIE, Mills-Packard Sulfuric Acid Chambers, *Chem. & Met. Eng.*, **44**, 728, (1937). For many improvements both in America and Europe, see Fairlie, "Manufacture of Sulfuric Acid," *op. cit.*, Chap. 9, etc.

[2] FAIRLIE, Building the World's Largest Mills-Packard Acid Plant, *Chem. & Met. Eng.*, **50**, No. 9, 103 (1943).

Gay-Lussac towers operated in conjunction with several packed towers, built of acidproof masonry much like the Glover towers. In the Anaconda process the heat of reaction is removed by the circulation through the packed towers of precooled acid of such a concentration that it does not absorb the oxides of nitrogen. In this plant the rate of reaction is increased by raising the concentration of the oxides of nitrogen to about three times that in the ordinary chambers, that is to about 70 per cent (as $NaNO_3$) based on the sulfur burned. This plant operates with only 1 cu ft. of space per pound of sulfur burned per day.

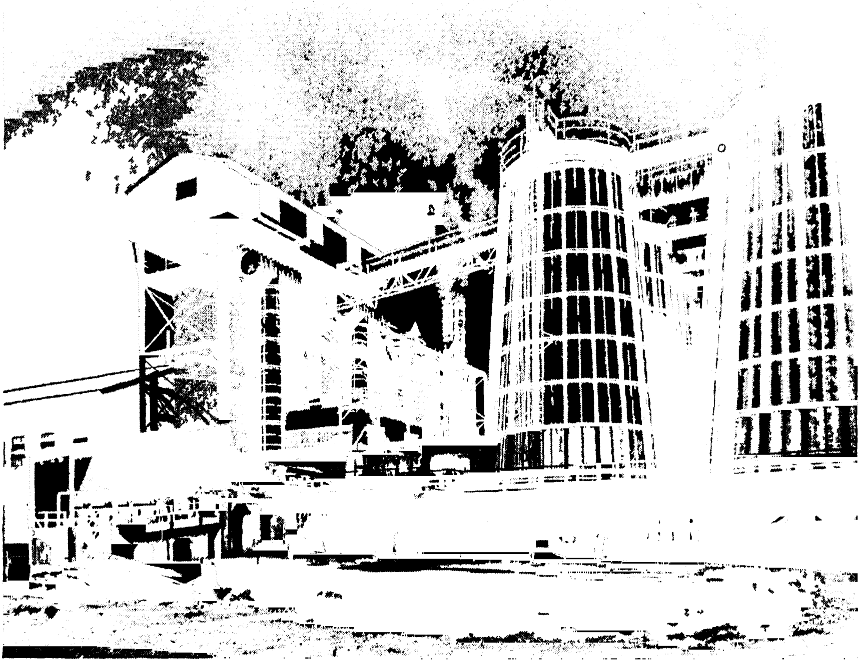


FIG. 8—World's largest Mills-Packard chamber sulfuric acid plant, located at Tampa, Fla The 20 lead chambers have a total of 440,000 cu ft There are two Glover and three Gay-Lussac towers (*Courtesy of U S Phosphoric Products Division, Tennessee Corporation*)

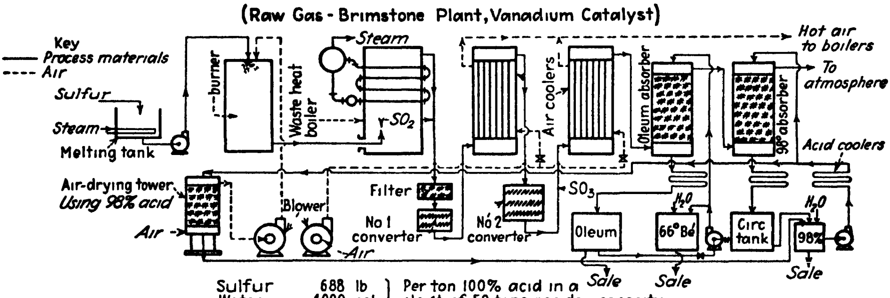
Other processes worthy of mention are the Falding process which consists of chambers about 75 ft tall followed by cooling towers; the Schmidel process in which the sulfuric gases are showered with nitrous vitriol; the pressure process in which the sulfurous gases are placed in a small tower which replaces the chambers; and the Watson process in which no towers are used and the acid is sprayed into chambers.

MANUFACTURE BY THE CONTACT PROCESS

Until 1900 no contact plant had been built in the United States. In Europe the contact method had become important by that time for the manufacture of oleums and high-strength acid needed for sulfonation, particularly in the dye industry. Oleums are widely employed at present in manufacturing the mixed (nitric-sulfuric) acid necessary for making nitro-organic compounds or the nitrate organic esters, so extensively used in the dye industry, plastics, and explosives. About 1930, American practice demonstrated that this newer process can compete with the chamber process in producing such acid as oil of vitriol.[1] One of the largest suppliers of sulfuric acid in the United States is not rebuilding its old chamber plants but is replacing them with contact units and making 66°Bé. acid by dilution of the 98.5 per cent acid. A typical flow sheet for one of the modern contact plants is shown in Fig. 9.

Unit Operations, Unit Processes, and Energy Changes.—The flow sheet of Fig. 9 can be divided into the following *unit sequences:*

Transportation of sulfur (or sulfides) to plant (Op.).
Melting of sulfur (Op.).
Pumping and atomizing of melted sulfur (Op.).
Burning of sulfur (or sulfide) (Pr).
Drying of combustion air (Pr.).
Recovery of heat from or cooling of hot SO_2 gas (Op.).
Purification of SO_2 gas (Op.).
Oxidation of SO_2 to SO_3 in converters (Pr.).
Heat transfer to secure good yields of SO_3 (Op.).
Absorption of SO_3 in strong acid, 98.5 to 99 per cent (Pr.).
Cooling of acid from absorbers (Op.).
Pumping of acid over absorption towers (Op.).



Sulfur	688 lb	Per ton 100% acid in a plant of 50 tons per day capacity
Water	4,000 gal	
Electricity	5 kw hr	
Direct labor	064 man hr	
Steam*	200 lb	

Note Investment in such a plant $ 200 000 in 1940, for a purification system (pyrites) add $100,000

*Waste heat boiler will furnish up to 2,000 lb steam

FIG. 9.—Sulfuric acid manufacture by the contact process.

The energy evolved by the oxidation of sulfur to sulfur dioxide and from sulfur dioxide to sulfur trioxide has frequently been partly wasted in air coolers and partly utilized to raise the sulfur dioxide to reaction temperature in the converters. In Fig. 9, the heat of combustion of sulfur is partly utilized by a waste-heat boiler to generate steam for melting the sulfur and for power purposes around the plant. In some other plants (Monsanto particularly) that part of the heat of reaction not required for converter temperature control is saved by "inter" and "after" cooling in waste-heat boilers, thus replacing the air coolers shown in Fig. 9.

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[1] COBLEIGH, Contact Sulfuric Acid Plant, *Ind. Eng. Chem.*, **24,** 717 (1932); DINSMOOR, A Modern Contact Sulfuric Acid Plant, *Trans. Am. Inst. Chem. Engrs.*, **26,** 158 (1931).

Reactions.—The reactions are

$$S + O_2 \rightarrow SO_2; \qquad \Delta H = -70{,}900 \text{ cal.}$$
$$2SO_2 + O_2 \rightleftarrows 2SO_3; \qquad \Delta H = -45{,}900 \text{ cal.}$$

The oxidation of sulfur dioxide in the converters of the contact plant is a very good example of the many industrial applications of the principles of physical chemistry. As shown above, the reaction from SO_2 to SO_3 is an exothermic reversible reaction. The equilibrium constant for this reaction calculated from partial pressures according to Guldberg and Waage's law of mass action may be expressed as

$$K_p = \frac{p^2_{SO_3}}{p^2_{SO_2} \times p_{O_2}}$$

Values for this expression have been calculated based on p in atmospheres and are presented here in Table 5, and are constant for any given temperature.

TABLE 5.—EQUILIBRIUM CONSTANTS FOR SULFUR DIOXIDE OXIDATION[a]

Temperature, °C.	K_p
400	397
500	48.1
600	9.53
700	2.63
800	0.915
900	0.384
1000	0.1845
1100	0.0980

[a] BODENSTEIN and POHL, Gleichgewichtsmessungen an der Kontaktschwefelsaure., *Zeit. Elektrochem.*, **11,** 373 (1905); FAIRLIE, "Manufacture of Sulfuric Acid," p. 42, Reinhold Publishing Corporation, New York, 1936. See "Rogers' Manual of Industrial Chemistry," 6th ed., pp. 269–276, 311–321, D. Van Nostrand Company, Inc., New York, 1942.

From these values and from Fig. 10, it is apparent that the conversion of the sulfur dioxide decreases with an increase in temperature. For that reason it is desirable to carry out the reaction at as low a temperature as practicable. At 400°C., where from Fig. 10 the *equilibrium* condition is seen to be very favorable, being almost 100 per cent, the *rate* of attainment of this equilibrium is slow. The rate at 500°C. is 40 times as fast as that at 400°C.; at 550°C. it is much faster. Since the reverse reaction, $2SO_3 \rightarrow 2SO_2 + O_2$, does not become appreciable until 550°C., it would seem advisable to run the reaction initially at this temperature in order to get as much conversion as possible to take place quickly.[1] There is here a conflict between the favorable conversion equilibriums at lower temperatures and the favorable rates at higher temperatures.

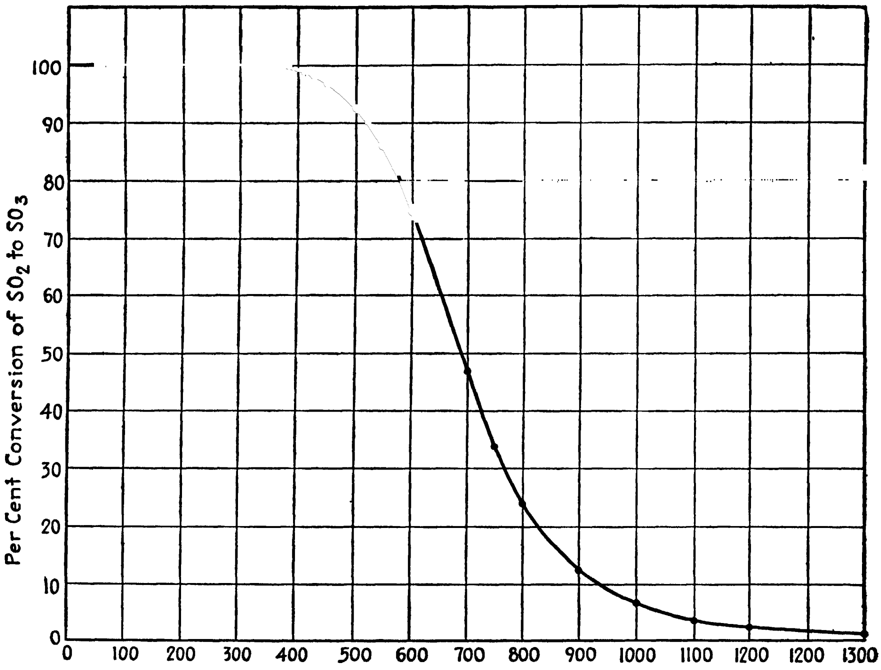

FIG. 10.—Equilibrium-temperature relation for SO_2 conversion to SO_3. (*Courtesy of International Correspondence Schools.*)

The actual procedure in a contact plant takes advantage of both the rate and equilibrium considerations by first passing the gases over a part of the catalyst at about 575°C. where the rate is high until about 80 per cent of the sulfur dioxide is converted. Then the gas, before it passes over the remainder of the catalyst, is cooled in a heat exchanger or in a waste-heat boiler, until the temperature of the gases passing over the last portion of the catalyst is only around 450°C. The yields using this procedure are over 97 per cent and the reaction rate is very rapid. Figures 11, 12, and 13 illustrate how these conditions are applied in practice and how the heat of reaction is used.

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[1] LEWIS and REIS, Influence of Reaction Rate on Operating Conditions in Contact Sulfuric Acid Manufacture, *Ind. Eng. Chem.*, **17**, 593 (1925).

By rewriting the expression for K_p in terms of mole fractions and total pressures, we have

$$K_p = \frac{N \times n_{SO_3}^2}{n_{SO_2}^2 \times n_{O_2} \times P}$$

where n = number moles of each component.
N = total moles.
P = total pressure.

By rearranging, we obtain

$$n_{SO_3}^2 = \frac{n_{SO_2}^2 \times n_{O_2} \times K_p \times P}{N}$$

From this expression it may be seen that an increase either of sulfur dioxide or of oxygen[1] will increase the formation of sulfur trioxide, thus illustrating the law of mass action. It should be borne in mind that in the burner gas, if the concentration of oxygen increases, that of the sulfur dioxide decreases and vice versa. An increase of pressure, according to the law of Le Châtelier, would also increase the yield of the sulfur trioxide, but the effect is so small and costly that it is not taken advantage of industrially. The fact that the moles of sulfur trioxide formed at equilibrium are inversely proportional to N, the total moles, shows that if the mixture of gases going through the converter were diluted with an inert gas, such as nitrogen, the yield of sulfur trioxide would be decreased.[2]

Catalysts.—It should be remembered that in all catalytic reactions, the only function of the catalyst is to increase the rate of the reactions. The catalyts that are of interest for the production of contact sulfuric acid are platinum and vanadium pentoxide. For many years platinum was the only catalyst used industrially, but shortly after the First World War, vanadium gained much ground and there soon arose a sharp rivalry between the advocates of these two. It was not until 1929, however, that many plants began operating on the vanadium catalyst mass. During the years that the vanadium catalyst was developing, the efficiency of the platinum catalyst was more than doubled. This fact was responsible for a continued employment of the platinum catalyst.

Platinum Catalysts.—Platinum is applied as a catalyst on several carriers, the most important being silica gel, calcined magnesium sulfate, and asbestos. The carriers for this catalyst must be porous, have a large surface area, be chemically inert to the gases at high temperatures, be refractory enough to stand the high temperatures, and be strong enough to resist the jars and strains placed on them.

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[1] MILES, "Manufacture of Sulphuric Acid (Contact Process)," D. Van Nostrand Company, Inc., New York, 1925; FAIRLIE, "Manufacture of Sulfuric Acid," *op. cit.*, p. 341.

[2] As is true with all phases of sulfuric acid manufacture, Fairlie, *ibid.*, should be consulted; chaps 12 and 14 partly elaborate on the subject here presented. For a most excellent presentation of the theory of the contact reaction see pp. 269–276, 311–321, of Rogers, *op. cit.;* this reference is written by Grosvenor and Phillips.

Platinized asbestos is prepared by impregnating specially treated asbestos with a solution of platinic chloride to give a mass that contains from 6 to 10 per cent platinum. The usual platinized asbestos requires 5 to 7 troy ounces of platinum per ton of 100 per cent sulfuric acid per 24 hr. Recently there has been produced a special type of "low-ignition" platinized asbestos which is capable of producing the same amount of sulfuric acid with only 2 to 3 troy ounces of platinum. The impregnation of calcined magnesium sulfate with platinic chloride is done in analogous manner and requires about the same amount of platinum as the ordinary platinized asbestos.

One of the most recent contact catalysts is platinized silica gel.[1] It is prepared by spraying a hardened silica gel with a solution of ammonium chloro-platinate. This catalyst usually contains about 0.1 per cent platinum, gives conversion efficiencies of about 96 per cent, and requires only from 1.5 to 3.5 oz. of platinum per daily ton of 100 per cent sulfuric acid.

Vanadium Catalysts.—Soluble compounds of vanadium deposited on a carrier were proposed as a catalyst for production of sulfuric acid as early as 1895, but it was not until 1926 that a catalyst of vanadium was used in the American sulfuric industry. The early vanadium catalysts, known as *Monsanto mass* and the *Selden mass*, are prepared from ammonium vanadate or vanadium pentoxide and a carrier such as a zeolite, other base exchange substances, or kieselguhr.[2] The vanadium catalysts give high conversions of 97 to 98 per cent.

The advantages[3] claimed for platinum are that 90 per cent of the original metal may be recovered, the operating cost is less (mainly owing to the fact that there is a royalty charge for the vanadium catalyst), and the initial capital cost of the plant is less because gases with higher proportions of sulfur dioxide (8 to 10 per cent) may be used. The disadvantages of platinum are that it suffers a decline of activity with use, the life of the catalyst is shorter, it is subject to poisoning under some conditions, and it is very difficult to handle because it is so fragile. The advantages claimed for vanadium masses are that they have a higher conversion efficiency maintained for a longer period than platinum, the catalysts are immune to poisoning (not now of any great importance), the vanadium mass is less troublesome during operation, it is easier to handle, and there is a lower initial cost for a vanadium catalyst. The disadvantages of vanadium are that it handles a lower sulfur dioxide (7 to 8 per cent) content gas, it cannot be overloaded as can platinum, and it has no salvage value when worn out.

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[1] PATRICK, U.S. Pat., 1297294.

[2] Patent and literature references to catalysts, together with abstracts therefrom, and testimony in the various law suits are summarized by Fairlie, *op. cit.*, Chap. 17.

[3] THOMPSON, Platinum vs. Vanadium Pentoxide as Catalysts for Sulfuric Acid Manufacture, *Trans. Am. Inst. Chem. Engrs.* **27**, 264 (1931); also FAIRLIE, *ibid.*, **Chaps. 17 and 18.**

It should be mentioned that, among the users of the vanadium catalyst in brimstone plants, no dissatisfaction has been found. It is probable that, when the royalty charged on the vanadium catalysts is reduced, sulfuric acid can be produced more cheaply with this catalyst than with platinum.

CONTACT PROCESS EQUIPMENT

Fairlie in his book on sulfuric acid manufacture details the many variations in the equipment employed that appeared to his date of publication (1936). Perry[1] lists the materials which withstand sulfuric acid of different concentrations and at various temperatures and of which the equipment is constructed. The more important improvements are presented in the following sections.

Treatment of the Burner Gas.—The sulfur dioxide burner gas for the contact process may contain, in addition to dust, carbon dioxide, nitrogen, and oxygen, such impurities as arsenic, chlorine, and fluorine. The last three impurities are present only when pyrite is burned. To prevent corrosion from the burner gases and to add the water more advantageously to the absorber acid, it is now customary, as shown in Fig. 9, to dry the air for burning the sulfur or a sulfide. Such drying is done in towers usually with 95 to 98 per cent sulfuric acid. The burner gas has much of its heat removed in waste-heat boilers for the generation of steam. If a sulfide is burned, an efficient dust collector and acid washing towers may be added. The sulfuric acid wash removes halogens.

Preheaters and Coolers.—Before the gases can be taken to the converter, they should be heated to increase the speed of the reaction. Since the converted gases should be cooled on issuing from the converter, all plants use the heat from these gases to preheat the gases traveling to the converter. These heat exchangers usually consist of large vertical cylinders containing many small tubes. The sulfur trioxide gas passes downward through the tubes while the sulfur dioxide gas surrounds the tubes and passes upward against them. In some cases baffles are provided to change the direction of the gases so that better heat transfer will be obtained. Several heat exchangers may be used and many complicated designs have been introduced.

Converters.—Converters[2] are of two broad types: two-stage or multipass converters with outside heat exchangers or by-product boilers

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[1] *Op. cit.*, p. 2100.

[2] DuBois and Harney, Contact Sulfuric Acid Converters, *Ind. Eng. Chem.*, **24**, 1091–1096 (1932).

(Figs. 9 and 13), and a converter that is a combination converter and heat exchanger (Figs. 11 and 12). The first stage or the first converter oper-

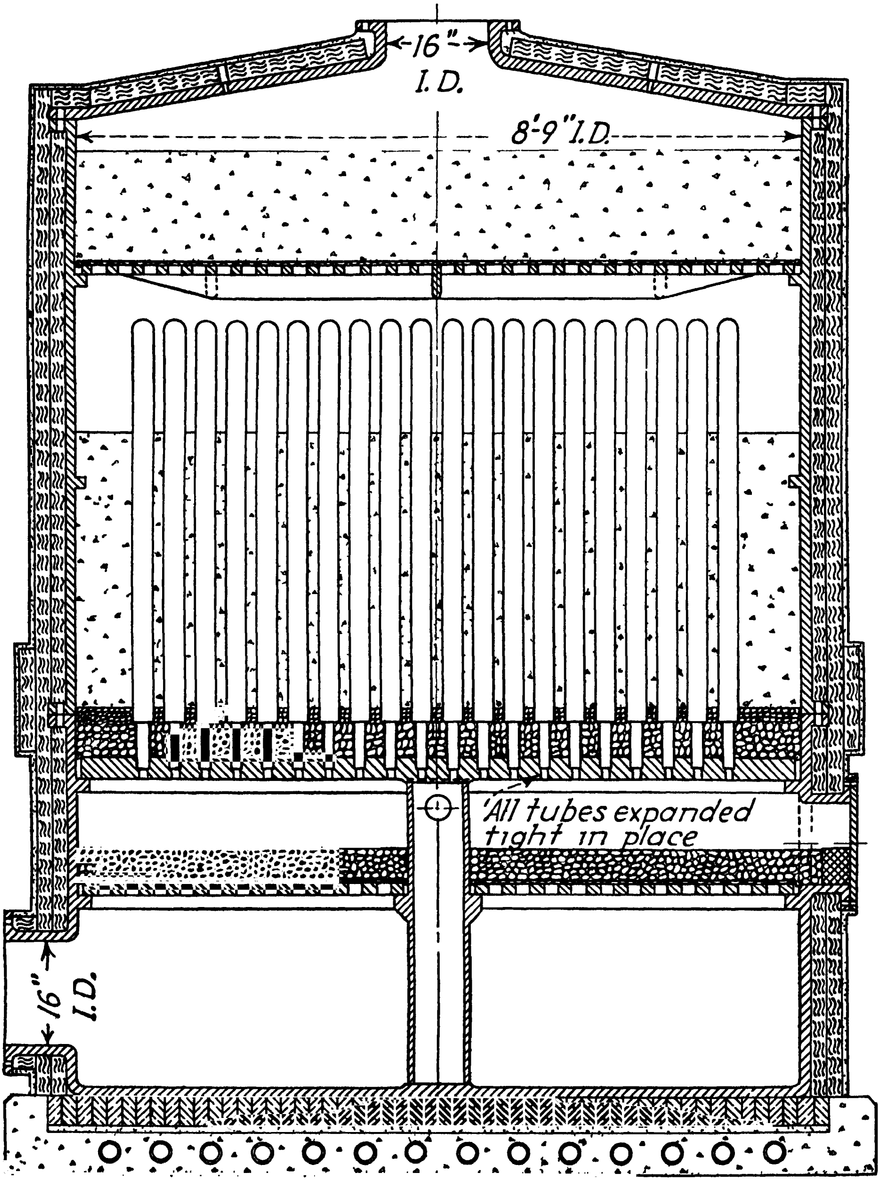

FIG 11.—"Chemico" Selden converter for sulfur trioxide using vanadium pentoxide. (*Courtesy of Chemical Construction Corporation.*)

ates at a higher temperature up to from 500 to 600°C. to ensure a rapid attainment of a moderate conversion equilibrium. The second stage or the second converter is controlled to a lower temperature of around 400 to 450°C. where the rate is slower but the conversion is higher. This combination results in a high over-all efficiency. Other factors in the conversion are the time of contact of the gas with the catalyst and the activity of the catalyst.

The multipass type generally consists of a primary converter which contains about 30 per cent of the total amount of catalyst. The secondary has the remaining portion of the catalyst divided into several layers. These are usually operated in conjunction with two heat exchangers or two by-product boilers. Burner gas, partly cooled by the by-product boiler, passes downward and in the top of the primary converter. The gas is about 80 per cent converted here and is heated to the higher temperature. It flows to the intercooler or heat exchanger and enters the top of the second converter at the lower temperature passing through the catalyst layers where the conversion is brought to about 96 or 97 per cent (see Fig. 9). The gas passes through the after-cooler or heat exchanger and then to the absorber.[1]

The second type of converter passes the incoming sulfur dioxide gas entering at about 260°C., upward through inner pipes and downward through the outer concentric pipes embedded in a deep layer or 60 per cent of the catalyst as shown by Figs. 11 and 12. This lower catalyst bed is maintained at 570 to 595°C. and accomplishes 85 per cent of the conversion. The sulfur dioxide first has its temperature raised in the outer pipe; it then enters the catalyst bed, oxidizes, and liberates heat with a further rise in temperature. This rise is checked and reduced by the continued

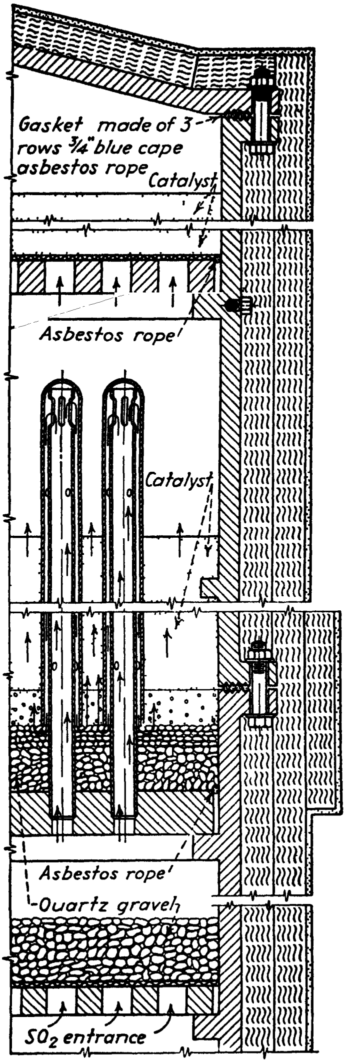

FIG. 12.—Detail of heat exchange in "Chemico" converter. (*Courtesy of Chemical Construction Corporation.*)

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[1] *Cf.* ANON, Contact Acid from Pyrites, *Chem. & Met. Eng.*, **46**, 477 (1939) for a pictured flow sheet of a multipass plant with different arrangement of gas treatment.

upward flow through the catalyst bed and above it of the partly converted sulfur dioxide (counter to the downflow of the incoming sulfur dioxide in the pipes). The partly converted sulfur dioxide continues to rise upward at its lowered temperature through the second layer of catalyst, maintained at 460 to 475°C., and is there converted to sulfur trioxide up to 97 per cent. This hot gas passes to the after-cooler or boiler and then on to the absorbers at a temperature of around 140°C. The figures, just cited, are for a Chemico vanadium converter which has an ignition temperature of about 400°C., hence the gases must contact the catalyst above this temperature to avoid cold spots.

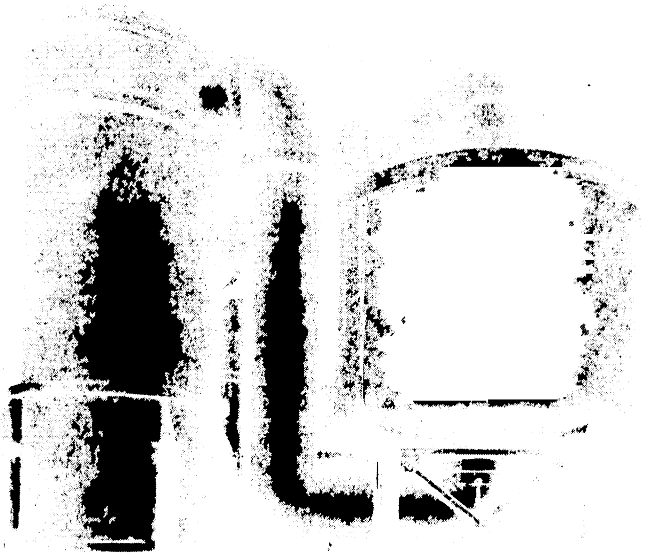

FIG. 13.—Heat exchanger and secondary converter of the Monsanto multipass system (*Courtesy of Monsanto Chemical Company*)

The advantages[1] of the first type are the lower cost of construction, greater accessibility for repair, the use of less catalyst, less power for the movement of gases, and ease of adaption to gases of varying sulfur dioxide content. The advantages of the other type are that it occupies less ground space and that the heat-exchanger tubes are not subject to rupture by buckling or stretching.

Sulfur Trioxide Absorbers.—It has been known for a long time that a concentration of acid between 98.5 and 99 per cent sulfuric acid is the most efficient agent for absorption, probably because acid of this strength has a lower vapor pressure than any other concentration. Hence acid of this strength is used for the final absorber before the waste gas is vented to the atmosphere. Water cannot be used because an acid mist is formed by the direct contact with the sulfur trioxide which is almost impossible to absorb. Since the absorbing acid is continuously becoming more concentrated, it is necessary to provide some means for diluting that part of the acid discharged from the final absorber which is to be recirculated. Also, the absorbing acid must be cooled. The diluting of the recirculating acid is done by adding spent or dilute sulfuric acid or water in the amount required, withdrawing from the system any excess acid for sale.

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[1] FAIRLIE, *ibid*, p. 382, also pp. 365–383, quoting DuBois and Harney, *op. cit.*

The 20 per cent oleum is made in the oleum absorber, as shown in Fig. 9, by passing cooled 99 per cent acid over this tower. If an oleum of 60 to 70 per cent is wanted, it may be prepared by distilling the 20 per cent oleum in steel vessels. The trioxide driven off is absorbed in 20 per cent oleum in water-cooled vessels equipped with a mechanical stirrer.

Although bubble-cap towers have been used to absorb sulfur trioxide, the most common type is the packed steel towers lined with acidproof masonry. Unlined towers are now being employed where cast iron is used for the 98 to 99.5 per cent acid and steel for the oleums. The packing generally consists of chemical stoneware,[1] though at times lumps of quartz or coke have been used. The gas enters the bottom and leaves by a flue out of the top. It has been found that a tower 6 ft. in diameter and 24 ft. high will absorb ¼ ton of sulfur trioxide per hour while recirculating 10 tons of acid. Newer developments in the latest plants are towers capable of absorbing 4 tons of sulfur trioxide while fed with a 110 tons of recirculating acid per hour. At least two absorbers are used, connected in series. In the first tower 20 per cent oleum is usually made. In the second tower, 98 per cent sulfuric acid is made.

Problems

1. An iron pyrite has the following composition: Fe, 40.0 per cent; S, 43.6 per cent. This pyrite is burned with air 100 per cent in excess of that required to burn all the iron to Fe_2O_3 and all the sulfur to SO_2. Assume that no SO_3 is formed in the furnace. After the gases formed have passed through the converter, 95 per cent of the SO_2 is oxidized to SO_3. What will be the composition of the gases entering and leaving the converter?

2. Oxides of nitrogen may be produced by treating crude $NaNO_3$ with sulfuric acid or by the oxidation of ammonia. How many pounds of 66° Bé. sulfuric acid and 95 per cent sodium nitrate must be used to yield the equivalent of the oxides of nitrogen produced by oxidizing 1 lb. of anhydrous ammonia?

3. A typical analysis of an Illinois coal shows it to contain 2.99 per cent S, 66.5 per cent C, 4.26 per cent H, and the remainder noncombustibles. A large power

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[1] Perry, *op. cit.*, pp. 1199*ff*.

plant burns 500 tons of this coal per day with 40 per cent excess air. What will be the composition of the stack gas in percentage SO_2? If a plant was installed to recover this sulfur dioxide, how many cubic feet of gas (at 300°F. and 750 mm.) would have to be scrubbed per minute? Assuming a recovery of 50 per cent of the sulfur fired in the form of SO_2, how many tons of sulfuric acid (66°Bé.) could be produced as a by-product of this plant in a year?

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CHAPTER XX

NITROGEN INDUSTRIES

Man must feed nitrogen back into the soil or face a decrease in his supply of food. However much this latter was feared at one time, the chemists and the chemical engineers 25 years ago found out how to make nitrogen derivatives out of air in an economical way. The first successful process—the arc process—required much cheap electrical energy. However, the present solution of the nitrogen-fixation problem came from reacting nitrogen with low-cost hydrogen to make ammonia under conditions requiring low power demands and low conversion expense. This made the arc process obsolete. Ammonia has now become one of our heavy chemicals produced in an enormous tonnage throughout the globe and at such low prices as to dominate the world supply of nitrogen fertilizers and most nitrogen compounds. It is probable that this is one of the most important chemical engineering achievements of history.

Historical.—Priestley observed that an electric spark passed through air confined over water caused a lessening in gas volume and acidification of the water. A few years later, in 1780, Cavendish repeated Priestley's experiments and found that nitrites and nitrates were formed if the experiment was carried out over an alkaline solution. With the lowered cost of electrical energy which came with the use of water power, interest in the arc method of nitrogen fixation was revived and was accompanied by the establishment of a successful arc process in Norway in 1904, known as the *Birkeland-Eyde* process. Here air was passed through a flaming electric arc at a very high temperature when a small percentage of the nitrogen was burned to NO. This nitric oxide was rapidly cooled successively in brick-lined iron pipes, steel boilers, and aluminum coolers, being oxidized to NO_2 at the lower temperatures. The initial cooling was rapid to prevent reversal. Other arc furnaces rapidly followed, but today the arc method is competitively uneconomical and is obsolete.

Attempts to produce cyanides of the alkaline earth metals as substitutes for the more costly alkali cyanides resulted in the discovery of the calcium cyanamide method of fixing nitrogen. The cyanamide, as such, is a fertilizer but, by further treatment, may be transformed into a cyanide or into numerous other nitrogen-containing chemicals such as guanidine.

The direct ammonia method was long in developing but it now holds the paramount position. It was the researches of Haber, Nernst, and *their coworkers that laid the real foundation for the present exceedingly* important synthetic ammonia industry and, in the years 1904–1908, equilibrium data for the ammonia-nitrogen-hydrogen system were established with fair accuracy over considerable ranges of temperatures and pressures. The development of a practical synthetic ammonia process was carried out through the efforts of Haber and Bosch with their coworkers, and the growth of this industry has continued since this beginning.

Curtis[1] describes various processes not now economical, such as the arc,[2] cyanide, and Serpek aluminum nitride procedure. The cyanamide and the ammonia manufacturing procedures are the present ones of technical importance for supplying the world with fixed nitrogen (Tables 1 and 2). These two will be described. The only plant in North America producing calcium cyanamide is at Niagara Falls, Canada, and is owned and operated by the American Cyanamid Company. It now has an annual capacity of 355,000 tons of calcium cyanamide, representing a fixation of 75,000 tons[3] of nitrogen per year.

Uses and Economics.—Table 1 outlines the respective power requirements and summarizes the costs of the synthetic processes that have been employed. The chemical nitrogen industries include not only the nitrogen fixed by man but also the by-product ammonia from coke ovens and such natural nitrogen deposits as Chile saltpeter, all subjected to manufacturing processes. Tables 2 and 3 summarize the situation prior to the Second World War. Although the synthetic ammonia controls the field, natural sources of nitrogen are still of tremendous importance[4] as Table 4 shows.

In the fiscal year 1929–1930 the total nitrogen used in fertilizers was 316,000 tons (N), of which 65 per cent was in mixed fertilizers and 35 per cent was used as materials. In the year 1931–1932 this had dropped to 182,000 tons (N), owing to the depression and a reduced demand for fertilizers. By 1935–1936 it had increased to 317,000 tons, 52 per cent in mixed fertilizers and 48 per cent as materials. The year 1937–1938 may be considered as free of war influence and probably representing a permanent minimum level of use. In that year United States agriculture used approximately 356,000 tons of nitrogen of chemical origin, industry used approximately 144,000 tons, and exports amounted to 43,000 tons. The total consumption of chemical nitrogen was 543,000 tons.

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[1] CURTIS, "Fixed Nitrogen," Reinhold Publishing Corporation, New York, 1932. This is an excellent book for this field and will be referred to frequently in this chapter.

[2] *Cf.* PERRY, *op. cit.*, pp. 2815 and 2821, for a short presentation of the arc processes.

[3] ANON., Production of Cyanamide, *Chem. & Met. Eng.*, **47**, 253 (1940). This article is illustrated.

[4] This matter is further discussed in Chemical Nitrogen, *U.S. Tariff Comm. Rept.* 114, pp. 72–75, 200–206, 1937. The statistical number (usually the February issue) of *Chem. & Met. Eng.* should be consulted. See Nitrogen Tables, *Chem. & Met. Eng.*, **48**, No. 2, 95–96 (1941).

TABLE 1.—ESTIMATED COST OF NITROGEN FIXATION BY VARIOUS PROCESSES,[a] PER TON OF 2,000 LB. OF PRODUCT OR OF NITROGEN CONTENT, AS SPECIFIED
(The prices quoted are those obtained in regions of the United States where specific processes are being or may be used)

Cost item	Direct synthetic ammonia process, with water-gas hydrogen, based on 200,000 short tons ammonia annual capacity		Cyanamide process, based on 350,000 tons cyanamide annual capacity		Arc process
	Ammonia	Nitrogen content of ammonia	Calcium cyanamide	Nitrogen content of cyanamide	Nitrogen, with 20 per cent as sodium nitrate and 80 per cent as nitric acid
Capital cost per ton	$155.00[b]	$188.00[b]	$85.00	$360.00	$600.00
Operating expense,					
Amortization of capital cost, interest, taxes charged at 15 per cent	$ 23.25	$ 28.20	$12.75	$ 54.00	$ 90.00
Power consumption, per ton.	1,250 kw.-hr. at $0.004 = $5.00	1,500 kw.-hr. at $0.004 = $6.00	2,120 kw.-hr. at $0.003 = $6.36	9,000 kw.-hr. at $0.003 = $27.00	61,000 kw.-hr. at $0.0015 = $91.50
Other operating and maintenance costs, including royalties	$ 26.75	$32.00	$12.35	$ 52.50	$ 60.00
Total estimated costs	$ 55.00[b]	$66.20[b]	$31.46	$133.50	$241.50

[a] Abstracted and modified from Table 6, pp. 46–47, Chemical Nitrogen, *U.S. Tariff Comm., Rept.* 114, 1937. (Power Consumption for 1 ton of nitrogen as cyanamide reduced from 12,000 to 9,000 kw.-hr.)

[b] The high plant capacity is in part responsible for low capital cost.

TABLE 2.—WORLD PRODUCTION OF CHEMICAL NITROGEN[a]
(In thousands of short tons by calendar years)

Type of production	1900	1913	1924	1929	1934
By-product....................	110.0	312.5	352.3	496.6	393.6
Ammonia and arc (early years)....	.....	24.2	355.5	1,102.1	1,331.9
Cyanamide....................	.....	42.0	120.5	250.7	238.5
Chilean nitrate.................	220.0	472.7	412.4	554.8	144.5
Total........................	330.0	851.4	1,240.7	2,404.2	2,108.5

[a] Abstracted from table, p. 7, Chemical Nitrogen, *U.S. Tariff Comm. Rept.* 114, 1937.

The imports for that year were about 192,000 tons. With due allowance for carry-over of stocks, it is apparent that United States production of chemical nitrogen had reached a level of between 350,000 and 375,000 tons of nitrogen per year, with some unused capacity above that figure.[1]

TABLE 3.—PRODUCTION OF CHEMICAL NITROGEN BY COUNTRIES
(In thousands of short tons by calendar years)

Producing country	1913	1924	1929	1934
Germany	131.6	470.7	889.9	462.5
Chile	476.7	413.3	556.0	141.7
United States	39.5	129.6	318.9	256.7
Great Britain	99.5	108.4	217.7	175.0
France	18.9	33.6	103.9	187.5
Japan	3.9	36.9	90.5	208.0
Norway	22.0	25.0	75.0	65.5
Italy	6.3	15.8	56.0	98.6
Belgium	10.9	13.9	44.2	109.8
Netherlands	1.6	7.9	13.5	62.9
Soviet Union	3.2	.7	5.3	45.0
All other countries	29.3	65.6	181.3	158.8
Total[a]	843.5	1,321.4	2,552.2	1,972.0

[a] The totals differ from those in Table 2 by a maximum of 6.9 per cent (1934). Based on table p. 7, Chemical Nitrogen, *U.S. Tariff Comm., Rept.* 114, 1937.

TABLE 4.—NITROGEN: BALANCE SHEET FOR THE UNITED STATES[a]
(Based on a total acreage of harvested crops in 1930 of 366,505,000 acres)

Nitrogen	Short tons	Nitrogen	Short tons
Losses from		Gains by	
Harvested crops	5,500,000	Bacterial fixation	3,000,000
Pasturage	1,500,000	Rainfall	1,300,000
Drainage	900,000	Fertilizers	400,000
Erosion	500,000	Total gain	4,700,000
Total loss	8,400,000	Annual deficit	3,700,000

[a] Data from G. H. Collings, "Commercial Fertilizers," p. 14, The Blakiston Company, Philadelphia, 1941.

CYANAMIDE

Cyanamide is an excellent alkaline nitrogenous fertilizer and an important raw material for further synthesis of nitrogenous compounds. For a fertilizer, the raw cyanamide is treated with 3 or 4 per cent of mineral oil to reduce the dustiness of the product, or it is granulated. The production of ammonia from cyanamide by treatment in an autoclave with steam is not now economical. Sodium cyanide is made from calcium cyanamide by fusing it with salt, carbon, and a little carbide followed by rapid chilling.

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[1] SMITH, New Horizons in Nitrogen, *Chem. Eng. News*, **21**, 215–216 (1943).

$$CaCN_2 + 2NaCl + C \rightarrow CaCl_2 + 2NaCN$$

Salt is used in excess and lowers the fusion point but cannot be leached out after the reaction. Hence the product is not pure and it is mixed with calcium chloride also, but it is suitable for the cyaniding of ores and for making into other compounds, such as sodium ferrocyanide.

$$6NaCN(CaCl_2) + FeSO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + Na_4Fe(CN)_6 + 2NaCl$$

The sodium ferrocyanide is recovered by evaporation and crystallization, after filtration from the gypsum precipitated by the soluble sulfate ions. Organic materials such as guanidine and dicyandiamide which are now of importance are based on calcium cyanamide as a starting material. Urea used to be made from cyanamide.

Manufacturing Procedures.—When pure nitrogen gas is brought into contact with finely ground carbide, 75 to 80 per cent CaC_2, at a temperature of 1600 to 1800°F., calcium cyanamide forms according to the reaction:[1]

$$CaC_2 + N_2 \rightarrow CaCN_2 + C \text{ (amorph.)}; \qquad \Delta H = -68{,}000 \text{ cal.}$$

This reaction is only 80 to 90 per cent complete because of unreacted and decomposed carbide. The commercial fertilizer cyanamide contains 22 per cent nitrogen, with lime, carbon, and some carbide as impurities (1 to 2 per cent). The calcium carbide is made at the cyanamide factory in 30,000-hp. three-phase furnaces, producing per charge 125 tons of

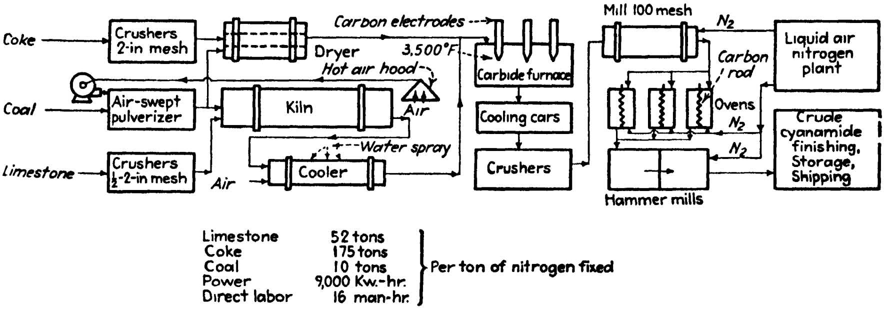

Fig. 1.—Flow sheet for making calcium carbide and calcium cyanamide.

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[1] Curtis, *op. cit.*, pp. 297*ff.*, for material and energy requirements for U.S. Nitrate Plant No. 2 in 1918 see pp. 307–310; Lee, Cyanamide Production Costs Reduced by Modern Equipment, *Chem. & Met. Eng.*, **38**, 564 (1931); Landis, Twenty-five Years Progress in the Cyanamide Industry, *Trans. Am. Electrochem. Soc.*, **51**, preprint, 1927. See general references at end of Chap. XVII, Electrothermal Industries.

carbide, by heating coke with quicklime as the following reaction shows and as is outlined in the flow sheet of Fig. 1, and described with more details in Chap. XVII.

$$CaO + 3C \text{ (amorph.)} \rightarrow CaC_2 + CO; \qquad \Delta H = +103{,}000 \text{ cal.}$$

Energy Changes, Unit Operations and Unit Processes.—As Table 1 shows, considerable over-all energy is needed, principally to secure the high temperatures required and to supply energy for the formation of CaC_2, which is more than 90 per cent of the total energy required to fix the nitrogen as cyanamide. The exothermic nature of the calcium cyanamide reaction helps the over-all energy balance. Coal is required to burn the limestone and to dry the raw materials.

The following *unit operations* (Op.) and *unit processes* (Pr.) are needed to commercialize[1] the reactions on which Fig. 1 is based.

Limestone, coal, and coke are pulverized, separately (Op.).

Limestone is calcined to quicklime (Pr.).

Coke is pulverized, dried, and mixed with quicklime (Op.).

Carbide is formed in an electric furnace at nearly 4000°F. and run out molten (Pr.).

Carbide is cooled, crushed, and finely ground (Op.).

Air is liquefied by compressing, cooling, and expansion (Op.).

Nitrogen is separated from oxygen by liquid rectification (Op.).

Calcium carbide is nitrified over the course of 40 hr. with 99.8 per cent nitrogen at 1800°F. (Pr.).

Calcium cyanamide is pulverized and treated with a small amount of water to hydrate residual CaO and CaC_2. It may be oiled to reduce dust (Op. and Pr.).

Ovens of the discontinuous type are the most common for the nitrification. They consist of a steel shell supported on a reinforced-concrete disk and are insulated with infusorial earth and lined with firebrick. Nitrogen is admitted through the bottom and through the side near the bottom. A carbon rod placed in the center of the oven serves as an electric resistance element to bring the carbide adjacent to it to the reaction temperature, after which the electricity is shut off and the exothermic nature of the reaction maintains the needed temperature. An oven taking a charge of 1,600 lb. of carbide requires a nitrification time of from 24 to 40 hr. depending upon such variables as oven dimensions and the physical condition of the charge. The resulting black powder containing 61 per cent $CaCN_2$ is crushed, finely ground, and treated with a spray of water to destroy the unconverted carbide (1.5 per cent), and to slake the quicklime.

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[1] For more details, see pictured flow sheet in Production of Cyanamide, *Chem. & Met. Eng.*, **47**, 253 (1940); ULLMANN, "Enzyklopaedie der technischen Chemie," vol. 2, 749–785; vol. 3, 1–37, Urban & Schwarzenberg, Berlin and Vienna, 1928–1932. The flow sheet given here, however, is quite exact, particularly regarding materials and power.

SYNTHETIC AMMONIA

Uses and Economics.—The product obtained is either an aqueous or an anhydrous liquid of great purity; the liquid or solution is suitable for ammonia refrigeration. For fertilizer use, it may be converted to ammonium sulfate by running the ammonia through a double decomposition reaction with carbon dioxide and ground gypsum (calcium sulfate) to form ammonium sulfate in solution with a precipitate of calcium carbonate. Ammonium phosphate is made by the direct combination of ammonia with phosphoric acid, but ammoniated superphosphates are more extensively used in fertilizers. The use of ammonia for oxidation to nitric acid is discussed later in this chapter. Urea is manufactured through ammonium carbamate from a heat and pressure reaction of ammonia and carbon dioxide. Ammonia finds much application also in the ammonia-chlorine antibacterial treatment of water, as a low-cost alkali, in the nitriding of steel, in the making of many organic chemicals such as aniline and β-naphthylamine, and as a source[1] (by cracking at 1700°F.) of free hydrogen (75 per cent) for welding, cutting, and annealing.

The product is handled and shipped in two forms: ammonia liquor and ammonia anhydrous. Commercial grades of the liquor usually contain 28 per cent ammonia. Shipment of anhydrous in this country is largely done in 50,000-lb. lots in special tank cars and in cylinders of 25, 50, 100, or 150 lb. Although Tables 2 and 3 indicate the extent of prewar commerce in ammonia, these figures are now being greatly exceeded.

Reactions and Equilibriums.—For the reaction

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 \rightarrow NH_3$$

the equilibrium constant is expressed as

$$K_p = \frac{p_{NH_3}}{p_{N_2}^{1/2} \times p_{H_2}^{3/2}}$$

The equilibrium constant can be calculated from known partial pressures as exemplified by Perry.[2] Since the volume of ammonia obtained is less than the combined volume of the nitrogen and hydrogen, according to the *principle of Le Châtelier*, a pressure increase will give a higher percentage of ammonia at equilibrium. The conversion percentage increases several fold as the pressure increases from 100 to 1,000 atm., but the percentage of ammonia in equilibrium with the reacting gases decreases *continually with the temperature rise up to and including 1000°C., above* which direct equilibrium determinations have not yet been made (see Fig. 2). As is apparent from the ammonia data presented in the figure, the lower the temperature for a given pressure at which an ammonia converter can be run, the larger the possible percentage of ammonia in the ammonia-nitrogen-hydrogen mixture, but the longer the time required to attain equilibrium. Accordingly, temperatures in the converters are kept as low as is consistent with a sufficiently rapid reaction rate to be economical on the catalyst used and with the investment required.

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[1] Brandt, Cracked Ammonia, *Chemistry & Industry*, **48**, 186 (1941). Costs and procedures are given for producing 75 per cent hydrogen or practically pure nitrogen at less than half the cost from cylinders of compressed hydrogen or nitrogen.

[2] Perry, *op. cit.*, pp. 751, 763. See Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," p. 557, McGraw-Hill Book Company, Inc., New York, 1923, for plot of log *K* against reciprocal of absolute temperature and for general free energy equation.

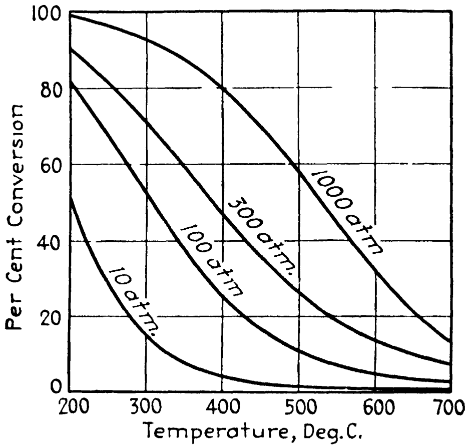

FIG. 2.—Percentage of NH_3 at equilibrium at various pressures and temperatures. (*After data in Table* 16, *p.* 152 *of Curtis, "Fixed Nitrogen," Reinhold Publishing Corporation, New York,* 1932.)

Rate and Catalysis of the Reaction.—To be economical, the rate of this reaction must be increased because hydrogen and nitrogen of themselves react very slowly. The solution of the commercial synthesis of ammonia rests upon efficient catalysts to speed up the reaction rate to an economical degree. Such catalysts[1] have been found in iron whose rate is promoted by the addition of small amounts of oxides of aluminum and potassium.

Space velocity is the number of cubic feet of exit gases, corrected to standard conditions (0°C. and 760 mm.), that pass over 1 cu. ft. of catalyst space per hour. The space velocity used in commercial operation differs considerably in different processes and in different *plants using the* same process. Although the percentage of ammonia in the gas stream issuing from a converter goes down as the space velocity goes up, the amount of ammonia per cubic foot of catalyst space per hour increases. However, a too high space velocity disturbs the thermal balance of a converter, involves increased cost of ammonia removal because of the smaller percentage present in the exit gases, and makes necessary the recirculation of large volumes of gas. Most commercial units use a space velocity of around 40,000.

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[1] EMMETT and KUMMER, Kinetics of Ammonia Synthesis, *Ind. Eng. Chem.*, **35**, 677 (1943). This article includes the newer Russian equations of Temkin and Pyzhev with much data and literature references.

Many reactions are known which occur as a result of one reacting constituent combining with the catalyst to form an intermediate compound that is capable of reacting with the second reacting constituent to form the product of the catalytic reaction and to regenerate the catalyst. Thus it is postulated that nitride formation is possible on the active iron atoms on the surface of the ammonia catalyst. Iron seems to be by far the most satisfactory *catalyst* material, though it seems to lose its activity rapidly if heated to temperatures above 520°C. The catalyst is promoted by metallic oxides, the activity being increased most by adding both an amphoteric oxide of a metal such as aluminum, zirconium, or silicon and an alkaline oxide such as potassium oxide. As P. H. Emmett[1] summarizes this, "The percentage ammonia in a gaseous mixture of pure 3:1 hydrogen-nitrogen gas passed over such a doubly promoted catalyst at 100 atm. pressure, 5,000 space velocity, and at 450°C., is 13 to 14 for the doubly promoted catalyst in contrast to 8 or 9 for the singly promoted one and to 3 or 5 per cent for the pure iron catalyst." The catalyst is prepared by burning the iron to the oxide, fusing it, and dissolving the promoters in the molten material. This material is crushed to the desired particle size and is strong enough to stand rough treatment without crumbling. The iron oxide is reduced to iron in the catalyst chamber by the nitrogen-hydrogen mixture, leaving a porous iron containing the various promoter materials. These catalysts are ruined by contact with many substances like phosphorus, arsenic, and sulfur; carbon monoxide greatly reduces their activity. Hence, much money must be spent in purifying the hydrogen and nitrogen for the ammonia synthesis.

Manufacturing Procedures.—There are numerous variations in pressure, temperature, catalyst, and equipment from the original Haber procedure, that have been put into practice in plants throughout the world. Table 5 summarizes these and includes the procedure for obtaining the hydrogen.

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[1] Curtis, *op. cit.*, p. 156. From p. 154 to p. 206, this book contains a most excellent summary of the theoretical and laboratory studies pertaining to the catalysis of nitrogen and hydrogen to form ammonia. *Cf.* Emmett, Studies on the Mechanism of Ammonia Synthesis over Iron Catalysts, *J. Chem. Education*, **7**, 2571–2583 (1930).

There is as much difference in the economic sources of hydrogen[1] as in any other variable. In those American plants where *by-product hydrogen* has previously been wasted, as from electrolysis of aqueous solution of salt, naturally this has been the cheapest source not only of the hydrogen but of the nitrogen by serving to burn the oxygen away from the nitrogen in the air. In other sections of the world where coal is comparatively expensive and electricity cheap, as in Norway and Italy, electrolysis of water has been employed. In this country, our chemical engineers have judged the *water gas and producer gas* reactions on coke followed by catalytic CO-H_2O shift conversion as the *cheapest long-term* source of hydrogen and nitrogen as well. This is described more in detail under the specific American procedures. But cheap fuel should also be available to make the steam needed for the CO-H_2O shift conversion-reaction as well as for power required for compression and pumping.

TABLE 5.—SYNTHETIC AMMONIA SYSTEMS

Designation	Pressure atmospheres	Temperature, °C.	Catalyst	Conversion percentage	Recirculation	Hydrogen and nitrogen
Haber-Bosch	200	550	Promoted iron	8	Yes	Water gas and producer gas
Nitrogen Engineering Corp., or American, or F.N.R.L.[a]	200–300	500	Doubly promoted iron	20–22	Yes	Water gas with producer gas or electrolytic by-product or natural gas
Claude	900–1,000	500–650	Promoted iron	40[b]–85	No	Liquefaction of coke-oven gas and air
Casale	600	500	Promoted iron	15–18	Yes	Various methods
Fauser	200	500	Promoted iron	12–23	Yes	Electrolytic, special cell
Mont Cenis	100	400–425	Iron cyanide	9–20	Yes	Electrolytic by-product or natural gas

[a] F.N.R.L., Fixed Nitrogen Research Laboratory.

[b] Conversion upon passage through a single converter. The 85 per cent is for conversion after passage through the series of converters.

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[1] CURTIS, *op. cit.*, pp. 206–222; FENSKE, Chap. 8, pp. 422–429; GROGGINS, "Unit Processes in Organic Synthesis," 2d ed., McGraw-Hill Book Company, Inc., New York, 1938; STENGEL and SHREVE, Hydrogenation: Economic Aspects, *Ind. Eng. Chem.*, **32**, 1212 (1940).

In certain sections of the country where it is abundant, *natural gas* has turned out to be the most economical source of hydrogen, particularly for the various wartime emergency ammonia plants. The investment is much reduced. From natural gas, hydrogen is made by two processes:

$$CH_4 + \Delta \rightarrow C + 2H_2 \tag{1}$$
$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{2}$$
$$CO + 3H_2 + H_2O \rightarrow CO_2 + 4H_2 \tag{3}$$

Reaction (1) is the patented Thermatomic cracking or pyrolysis process, described in Chap. IX as taking place at a high temperature or above 1600°F. and furnishing carbon for rubber manufacture as well as hydrogen for ammonia. As any residual methane is not poisonous to the ammonia catalyst but merely a diluent, it is kept from accumulating in the ammonia cycle by purging and burning under boilers. Natural gas[1] can also be cracked by passing through the bed of red-hot coke in a water-gas generator. Reaction (2) occurs at about 875°C. on an aluminum oxide base catalyst in high-chromium, high-nickel tubes heated on the outside to supply the necessary energy. The second phase[2] of this reaction takes place at about 450 to 500°C. over a ferrous oxide catalyst using excess steam. The carbon dioxide formed is washed out with water under pressure.

In Europe, hydrogen is obtained by *liquefaction* from *coke-oven* or *water gas*, but in America this is considered to be too costly. In 1934, it was estimated[3] that the world's source of hydrogen for ammonia comprised 57 per cent from water gas, 25 per cent from coke-oven gas, 16 per cent from electrolysis of water, and 2 per cent from other sources such as electrolysis of brine and natural gas. There are no later figures now available, but in America, natural gas[4] or other lower aliphatic hydrocarbons are very important as a source of hydrogen, not only for ammonia but for other hydrogenations leading to various petroleum products (*cf.* Chap. XXXVII).

Nitrogen Engineering Corp. System.—The system for ammonia synthesis developed by the Nitrogen Engineering Corp. (now a part of the Chemical Construction Corp. of the American Cyanamid Company)

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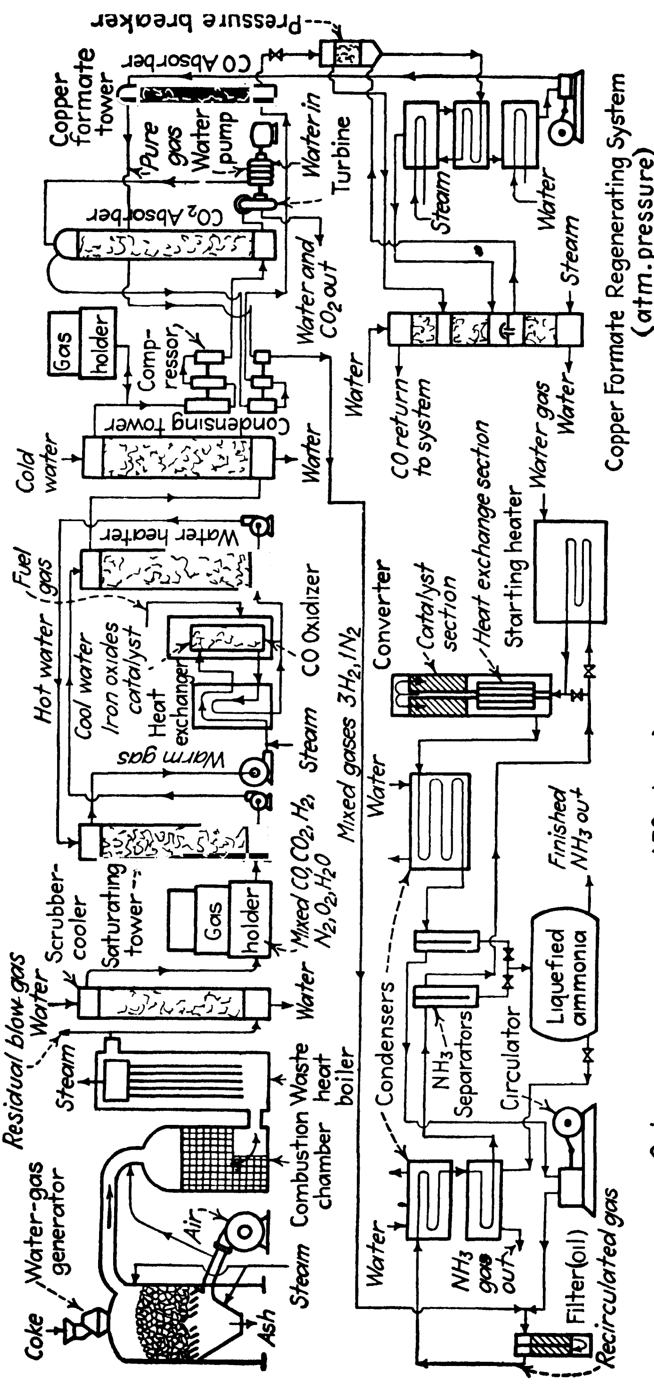
[1] ODELL, Reforming Natural Gas in Water Gas Generators, *U.S. Bur. Mines, Repts. Investigations*, 2973 (1929); U.S. Pat., 1726000 (1930).

[2] AUSTIN and DAY, Chemical Equilibrium and the Control of Furnace Atmospheres, *Ind. Eng. Chem.*, **33**, 23 (1941).

[3] Chemical Nitrogen, *U.S. Tariff Comm. Rept.* 114, (1937).

[4] DOTTERWEICH, Natural Gas as a Raw Material in the Production of Synthetic Ammonia, *Refiner, Natural Gasoline Mfr.*, **21**, No. 3, 51–55 (1942).



Coke	178	tons	Per ton liquefied NH$_3$
Water	31,000	gals	
Coal (steam and power)	2.3	tons	
Direct labor (about)	21.8	man-hr	

FIG 3 —Flow sheet showing ammonia synthesis (Nitrogen Engineering Corporation System)

is shown in the flow sheet of Fig. 3. Like all these ammonia syntheses, this one is based on the following reaction:[1]

$$N_2 + 3H_2 \rightarrow 2NH_3(g); \qquad \begin{aligned} \Delta H_{18^\circ\text{C.}} &= -22{,}000 \text{ cal.} \\ \Delta H_{659^\circ\text{C.}} &= -26{,}600 \text{ cal.} \end{aligned}$$

This reaction is highly exothermic and, consequently, the design of the converter should be such as to control the temperature at the point desired for the conversion deemed economical for the particular conditions chosen by the chemical engineers (*cf.* Fig. 2).

The Nitrogen Engineering Corp.'s system is a modified and improved Haber-Bosch system (*cf.* Table 5), and can best be presented by breaking down this flow sheet (Fig. 3) into the following coordinated sequences of *unit operations* (Op.) and *unit processes* (Pr.):

Coke is made into blue water gas by steam as the source of the hydrogen (Pr.).

Coke is converted by a little steam and air into producer gas as the source of the nitrogen (Pr.). The exothermic producer gas reaction permits, to a slight extent, the endothermic water-gas reaction. An alternate source of nitrogen is the "blow gas" from the water-gas generator. The proportions are properly adjusted to the desired ratio.

Heat is saved from hot gases (see Fig. 3) in waste-heat boiler (Op.).

After passing through waste-heat boiler, gases are further cooled and analyzed; gases are warmed and saturated with water vapor in a hot-water scrubber, treated with steam, heated further in exchangers, and passed over iron oxide catalyst to convert[2] $CO + H_2O$ into $CO_2 + H_2$; $\Delta H = -9{,}800$ cal. (Pr.).

The CO_2 and H_2 are cooled in the heat exchanger and cooling towers and conducted to gas holder which "floats" on the line (Op.). (Not shown in Fig. 3.)

To remove CO_2 from the original gas reactions and from the catalytic CO shift reaction, the gases are compressed to about 25 atm. and washed with water under this pressure (Op.). About 50 per cent of the energy required for this operation of raising the water pressure is recovered as shown in Fig. 3 in a water turbine and used over again for the same purpose. (The "mountain system" of energy recovery is shown in Fig. 4.)

The mixture of 3 parts of H_2 and 1 part of N_2 with residual CO (usually 2 per cent) is compressed with cooling to 200 atm. (Op.).

The CO and any small amount of O_2 are removed (to be put back into start of system) by solution in an ammoniacal cuprous formate solution which is regenerated by heat at atmospheric pressure and reused (Pr.).

The 3 to 1 hydrogen-nitrogen mixture, freed of its CO, is raised to the full compression of 300 atm. and mixed with the recompressed, recirculated gases. The gases then are passed through the oil filter and to the water-ammonia cooler-condenser for removal of residual ammonia (Op.).

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[1] PERRY, *op. cit.*, pp. 742–743 and 750 (equilibrium).

[2] *Cf.* PERRY, *op. cit.*, p. 751, for equilibrium calculations of this *shift* reaction.

In the converter, the gases are raised in a countercurrent heat exchanger to the reaction temperature and caused to react in the presence of the catalyst, after which the gases are cooled and some of the ammonia liquefied (Pr.).

Part of the gases is purged to prevent undue accumulation of diluents, such as methane or argon, and the rest is recompressed for recirculation (Op.).

The purge gas is burned.

One of the plants of the Nitrogen Engineering Corp. in the United States on by-product hydrogen experienced a catalyst life of about 3 years operating at 515°C. and 4,400 lb. pressure. The gas charged analyzed 72 to 73 per cent H_2, and from 15 to 24 per cent was changed to NH_3 per pass. A total of 80,000 cu. ft. of hydrogen was needed for 1 ton of ammonia.

In a modified Nitrogen Engineering Corp. system, Charles O. Brown[1] runs the blue water gas of the "make" cycle into a gas holder, for its hydrogen and carbon monoxide content. Part of the blow gas from the same water-gas set is led to a smaller holder for its nitrogen (with carbon dioxide) content. The two are metered in the proper proportion and put through the succeeding unit operations and unit processes as charted in Fig. 3. A *detailed* description with pictured flow chart is available[2] for the recently built (1943) T.V.A. ammonia plant which was designed under the leadership of Charles O. Brown and built by the T.V.A. engineers. The converter is of the laminated wall type.

The *American* system is a modified Haber-Bosch procedure, the details of which were researched and fully published by the Fixed Nitrogen Research Laboratory[3] at Washington, D.C. Much of the findings associated with the F.N.R.L. have been applied by the Nitrogen Engineering Corp.'s system. These work at 100 atm. above the Haber-Bosch or at 300 atm. and 475°C. A doubly promoted iron catalyst is used operating on very pure gas and hence with a relatively long life. This catalyst contains 1 per cent of potassium oxide and 3 per cent of aluminum oxide, based on the iron oxide originally charged. The promoters prevent sintering. A unique feature is the employment of an initial ammonia converter at a somewhat higher temperature, which has as its function the conversion of carbon-oxygen or carbon-oxygen-hydrogen compounds into water or hydrocarbons, as well as the removal of any sulfur compounds. Some ammonia is formed and condensed, taking out the impurities simultaneously. There are several small plants in the United States employing this system and operating on hydrogen by-product from electrolysis of salt. Part of this hydrogen (about 15 per cent) is used to burn the oxygen from air, leaving nitrogen which is mixed with three volumes of hydrogen, purified, compressed, heated, and reacted. The converter[1] is of chrome-nickel-vanadium steel containing the heat interchanger and the catalyst chamber. A certain amount of the gas in recirculation is purged to prevent accumulation of argon.

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[1] Consulting Chemical Engineer, New York City, and one of the original group that started the Nitrogen Engineering Corp.

[2] MILLER and JUNKINS, Nitrogen Fixation at the T.V.A. Ammonia Plant, *Chem. & Met. Eng.*, **50**, No. 11, 119 (1943); ANON., Ammonia Synthesis at T.V.A., *Chem. & Met. Eng.*, **50**, No. 11, 152 (1943).

[3] ANON., The American Process Nitrogen Fixation, *Chem. & Met. Eng.*, **30**, 948 (1924); CURTIS, *op. cit.*, pp. 237–239; ERNST, REED, and EDWARDS, A Direct Synthetic Ammonia Plant, *Ind. Eng. Chem.*, **17**, 775 (1925).

Haber-Bosch System.—The Haber-Bosch system is the basis of the industrial ammonia syntheses and is operated on a very large scale in Germany, particularly at Oppau and Merseburg, and with modifications elsewhere. It is understood that the very large plants of the Imperial Chemical Industries at Billingham, England, and that of the Allied Dye and Chemical Corp. (Solvay Process Co.) at Hopewell, Va., employ the Haber-Bosch procedures with minor modifications. This system started with about 30 tons of ammonia per day in 1913 and now produces in all probability around 3,000 tons per day in Germany alone. It operates at the comparatively low pressure of 200 atm. (and 550°C.) with from 5 to 10 per cent conversion (*cf.* Fig. 2). It has been fully described[2] and proceeds somewhat as the system depicted in Fig. 3. The catalyst is a promoted iron oxide. Because of the low pressure, the ammonia is somewhat more difficult to remove as a liquid so the reaction gases are washed with water, producing initially aqua ammonia from which anhydrous is manufactured. To convert the ammonia into more widely usable forms, especially fertilizer use, the I. G. Farbenindustrie A.-G. have commercialized a number of reactions, of which the one making ammonium sulfate is outlined under the description of this salt.

Claude and Casale Systems.—These two high-pressure procedures (1,000 and 600 atm.) are licensed in America to the Du Pont Co., whose large plant at Belle, W. Va., is understood to be a modification of both of these. The Claude process, operating at the high pressure of 1,000 atm., passes the gases through a number of B.T.G. metal[3] converters in series and does not need to recirculate them to secure a satisfactory yield of probably above 80 per cent. This simplification is secured at the cost of higher compression and shorter catalyst life at the high temperatures used. The Claude process like the Du Pont changes residual CO into CH_4 before entering the conversion chamber where the CH_4 is merely a diluent and not a catalyst poison as is true of CO.

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[1] PERRY, *op. cit.*, p. 2183, gives a diagram of this converter; *ibid.*, pp. 2167–2192, details the conditions and equipment used in high-pressure operations.

[2] CURTIS, *op. cit.*, p. 229; PARTINGTON, The Haber Process at Merseburg, *J. Soc. Chem. Ind.*, **40**, 144R (1921); WARDENBURG, High Pressure Applied to Manufacture of Things in Everyday Life, *J. Franklin Inst.*, **221**, 449–465 (1936).

[3] Composition probably: chromium 12 per cent, nickel 60 per cent, tungsten 2 per cent, iron 25 per cent, carbon 0.35 per cent.

The Casale system (*cf.* Table 5) is characterized chiefly by the design of the converter and condenser wherein some of the ammonia is left in the recirculated gases to temper or slow down the initial reaction in the catalyst chamber. Also, the entering gases are passed down in contact with the outside wall of the converter in order to keep its temperature below 400°C. and thus to eliminate the expensive nickel-chromium-tungsten alloy used in the Claude system.

Du Pont System.—The Du Pont much modified Claude-Casale system is outlined in Fig. 4. The plant is located at Belle, W. Va., on the banks of the Kanawha River where plentiful supplies of water and cheap coal are available. The coal is delivered by river barges. The Du Pont engineers are convinced that their cheapest[1] source of hydrogen for ammonia is basically from the water-gas reaction from coke. However, these engineers also process the coal gas for its hydrogen by liquefaction of its other constituents as is done in a number of European plants.

The ignited coke in the gas generators is blown with air, furnishing "blow-run gas" or "blow gas" rich in nitrogen and carbon dioxide. When this white-hot coke has steam and some air passed through it, "blue gas" is made, rich in hydrogen and carbon monoxide with some nitrogen. As this latter is an endothermic reaction (*cf.* Chap. VII), it must be succeeded by a "blow run." Thus alternately blowing air and steam through coke, the four gases are produced from which ammonia, ammonium carbonate, urea, alcohols, and dozens of other chemicals are made (*cf.* Fig. 1 in Chap. XXXIX). These gases are proportioned to get the mixture required for the product desired. In the case of ammonia, this is eventually 3 parts of H_2 for 1 part of N_2. However, the blue gas analyzing about 50 per cent CO, 40 per cent H_2, and 10 per cent N_2 must be purified of its sulfur. This is done by the Thylox process already described in Chap. VII.

As shown in Fig. 4 the Du Pont engineers remove the CO_2 by washing with water under 30 atm. pressure. They, however, have developed an economical method of recovering about 60 per cent of the energy in this high-pressure aqueous solution of the carbon dioxide. This is the so-called *mountain recovery* procedure in which the pressure in the water forces it 600 ft. up to the top of the mountain adjoining the Belle plant. When at the top of the mountain, the pressure having been expended in the work done, the CO_2 mostly escapes, the residual being blown out with air. This denuded water flows down again to the pumps but possessed of nearly 300 lb. actual pressure. Such a procedure also saves something in the cost in water purifying as the water is employed over and over again.

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[1] ANON., The Pressure Synthesis of the Du Pont Ammonium Corp., *Ind. Eng. Chem.*, **22**, 433 (1930).

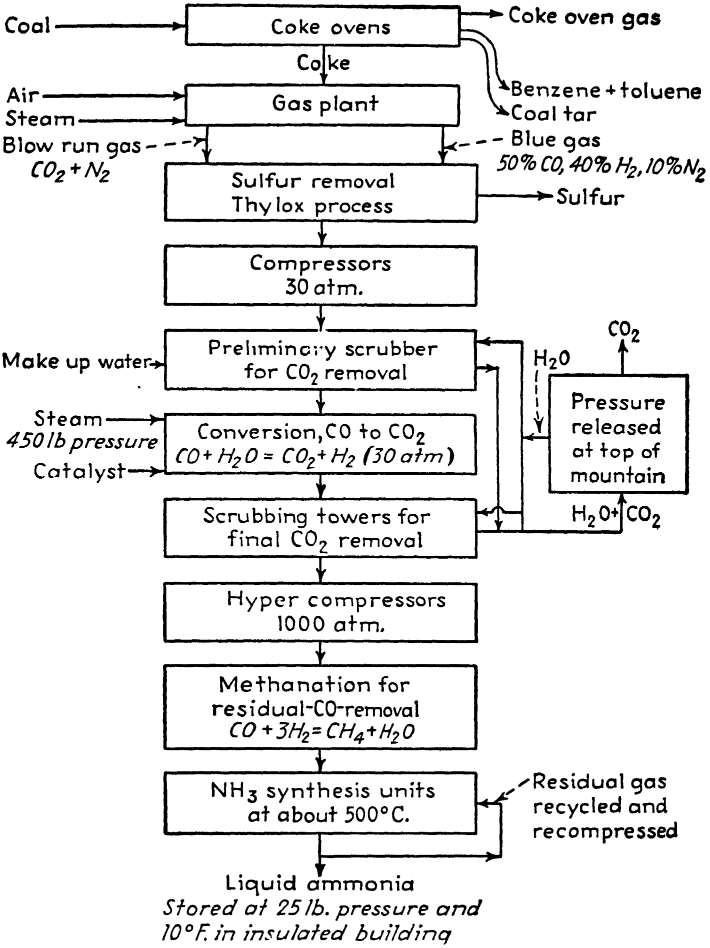

FIG. 4.—Flow chart for Du Pont ammonia synthesis from coal, air, and water. The blow-run gas and the blue gas are made from the coke by alternately blowing with air and steam.

Before wartime demands required an enlargement of this Du Pont plant, it had a gas plant sufficient in size to supply a city of over 2,000,000 inhabitants. It is obvious that it would not be economical to store more than a few minutes' supply. However, the various processes are so rapid, the coordination so accurate, and the control so exact, that

> . . . only thirty minutes are required for a unit of hydrogen leaving the coke bed in the water-gas generators to appear as its equivalent of ammonia or alcohols coming from the synthesis units. During the thirty minutes' ride taken by the gases in their journey at Belle, they are heated to 2400°F., washed and rewashed

with water and other liquids, cooled to −350°F., expanded to atmospheric pressure, compressed to 12,000 pounds per square inch, and passed over various catalysts.

To control and integrate these various steps has required a great deal of intelligence and stern vigilance, and the expenditure of over $1,000,000 in automatic instruments and devices.

Miscellaneous Ammonia Systems.—The Italian Fauser[1] procedure employs an electrically controlled converter at 200 atm. and 500°C. and works on electrolytic hydrogen generated in a special cell. For some of the foreign plants, the nitrogen is obtained by purification of the nitrogen from the exit gases arising from the air-ammonia oxidation procedure for nitric acid. At Trail, B.C., Claude liquid-air units furnish the nitrogen. This being a low-pressure system, the ammonia is frequently removed by water scrubbing, though the Trail plant employs pressure cooling first by water and next by ammonia refrigeration. The lowest pressure system is the *Mont Cenis* one, operating at 100 atm. and somewhat over 400°C. The catalyst is an iron-cyanide complex. This system is used by the Shell Chemical Co. at Pittsburg, Calif.

AMMONIUM SULFATE

Ammonium sulfate has long been an important nitrogen carrier for fertilizers. It has been made for many years by washing the ammonia out of coal gas (*cf.* Chap. VII) by passage through sulfuric acid[2] in a large lead-lined saturator. This process was used in Germany but has now been replaced by reaction with gypsum or anhydrite.

$$2NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2CO_3(aq)$$
$$(NH_4)_2CO_3(aq) + CaSO_4 \cdot 2H_2O \rightarrow CaCO_3 + 2H_2O + (NH_4)_2SO_4(aq)$$

The reaction takes place in from 6 to 9 hr., provided the gypsum is finely ground and kept in suspension. The solution is filtered and washed from the calcium carbonate and evaporated to crystallization.[3] The English plant at Billingham employs anhydrite. The calcium carbonate at the Haber-Bosch plant at Merseburg, Germany, is dissolved in nitric acid from air oxidation of ammonia, thus furnishing the fertilizer calcium nitrate[4] which is especially desired on acid soils.

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[1] For a flow sheet see *Chem. & Met. Eng.*, **38**, 628 (1931). This article describes with considerable exactness the procedures operating at Trail, B.C.

[2] Ernst and Edwards, A Sulfate of Ammonia Plant, *Ind. Eng. Chem.*, **19**, 768 (1927). This article includes heat of reaction of dilution of sulfuric acid as well as a description of equipment for a sulfate of ammonia plant from ammonia and sulfuric acid.

[3] *Cf.* Curtis, *op. cit.*, pp. 417, 418, for pictured flow sheet and further references.

[4] Curtis, *op. cit.*, p. 414.

AMMONIUM PHOSPHATES

These salts[1] are considered in Chap. XVIII. They are particularly valuable in the fertilizer field as they carry both NH_3 and P_2O_5.

AMMONIUM NITRATE

This is the simplest salt[2] to make as it can be derived from ammonia and its oxidation product, nitric acid.

$$NH_3(g) + HNO_3(aq) \rightarrow NH_4NO_3(aq); \qquad \Delta H = -20{,}600 \text{ cal.}$$

Around most explosive plants, any dilute nitric acid is thus neutralized, evaporated to 98 per cent ammonium nitrate, crystallized, and grained. Because of its humectant properties, the ammonium nitrate is crystallized under rolling motion to secure rounded grains of minimum surface in a special flat graining kettle. To reduce humectant qualities these rounded grains are coated with 0.3 per cent of a mixture of rosin, soft and hard paraffin, and finally with 1 per cent of finely ground calcium carbonate. This makes a free-flowing water-resistant noncaking ammonium nitrate very suitable for use in dynamite but still not sufficiently water-resistant to be employed generally in fertilizer mixes. However, double salts and mixtures are prepared in Europe and sold under various trade names as Leuna saltpeter, cal-nitro, and nitro-chalk. About 15,000 to 25,000 tons (Table 6) of ammonium nitrate are produced annually in the United States and about 4,000 tons are imported (peace demands). Under war demands, the production of ammonium nitrate has usually been greatly increased as this is the only substance of its general oxygen-carrying nature that can be safely mixed with T.N.T. Such mixtures are known

TABLE 6.—ESTIMATED UNITED STATES PRODUCTION OF SECONDARY NITROGEN PRODUCTS, DERIVED CHIEFLY FROM AMMONIA[a]

Product	Tons of Nitrogen
Nitric acid	30,000–45,000
Ammonium nitrate	15,000–25,000
Ammonium chloride	400– 7,500
Ammonium phosphate	1,500– 6,000
Ammonium carbonates	100– 350
Sodium nitrate	500– 1,000
Sodium cyanide	1,000– 2,500
Miscellaneous	1,500– 2,650
Total	50,000 90,000

[a] Chemical Nitrogen, *U.S. Tariff Comm. Rept.* 114, p. 197, 1937. Productions of many of these compounds are greatly increased during war years.

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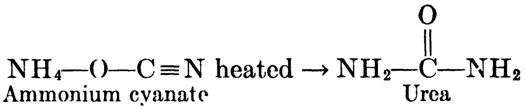
[1] CURTIS, *op. cit.*, pp. 419–427. *Cf.* FALK, German Ammonium Nitrate, *Chem. & Met. Eng.*, **48**, No. 2, 120 (1941).

[2] CURTIS, *op. cit.*, p. 412; WOODWARD, Significance of Ammonia in National Defense, *Chem. & Met. Eng.*, **48**, No. 2, 117 (1941).

as 50/50 or 80/20 amatol—the first figure referring to the percentage of ammonium nitrate. Foreign nations[1] *employ more ammonium nitrate* than does the United States, especially in fertilizers, though the present war has stimulated this use[2] here.

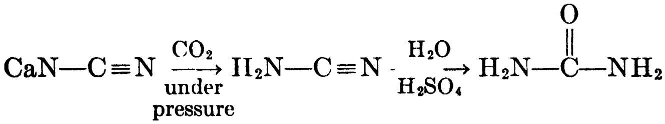
UREA

The synthesis of urea[3] by Wöhler in 1828 had a profound influence upon chemistry and upon civilization. Indeed it opened up the entire realm of synthetic organic chemistry and of organic technology with the thousands of products now so useful to man that it would be difficult to picture our modern daily living without them. Wöhler's synthesis may be written



$$\underset{\text{Ammonium cyanate}}{NH_4{-}O{-}C{\equiv}N} \text{ heated} \rightarrow \underset{\text{Urea}}{NH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2}$$

For 100 years, this epoch-making compound had a very minor industrial application, being used to the extent of a few thousand pounds per year, as an antiacid and stabilizer in celluloid (*cf.* Chap. XXXV). For this purpose it was made by the acid hydrolysis[4] of calcium cyanamide.



$$CaN{-}C{\equiv}N \xrightarrow[\text{under pressure}]{CO_2} H_2N{-}C{\equiv}N \xrightarrow[H_2SO_4]{H_2O} H_2N{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2$$

In recent years, the Du Pont chemical engineers have industrialized at Belle, W. Va., the very simple reaction[5] from low-priced materials, following prior work in Germany:

$$CO_2 + 2NH_3 \rightarrow \underset{\text{Ammonium carbamate}}{NH_2CO_2NH_4} \rightarrow \underset{\text{Urea}}{NH_2CONH_2} + H_2O; \quad \Delta H \text{ at } 150°\text{C.} = -7{,}900 \text{ cal}$$

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[1] Falk, German Ammonium Nitrate, *Chem. & Met. Eng.*, **48,** No. 2, 120 (1941); Anon., Ammonium Nitrate in Italy, *Chem. & Met. Eng.*, **48,** No. 2, 121 (1941). Compare the last reference and various articles by Fauser describing his pressure neutralizations of nitric acid by ammonia by which over 600 tons of ammonium nitrate are made per day in Europe.

[2] Smith, Ammonium Nitrate in Mixed Fertilizers, *Chem. Eng. News*, **21,** 2100 (1943).

[3] Krase in Chap. 13, pp. 337–365 of Curtis, *op. cit.*, reviews this most important synthesis with many literature references. The physical chemistry of the various reactions is particularly well presented.

[4] McBride, Manufacture of Fertilizer Urea on a Tonnage Basis, *Chem. & Met. Eng.*, **32,** 791 (1925).

[5] *Cf.* Krase, *ibid.*, pp. 359–363, for a very exhaustive study of the energy factors in these reactions. The ΔH given pertains only to the change from the ammonium carbamate. A flow sheet and fuller description are presented in Groggins, *op. cit.*, p. 358.

The carbon dioxide and the ammonia in excess are reacted through several hours in the liquid phase under pressure (100 atm.) and heat (190°C.) The process is operated continuously and with about 80 per cent conversion. Corrosion[1] has been particularly bad and has been overcome by using silver to line the autoclaves. The CO_2 and NH_3 are both produced ~~in the same plant~~ (*cf.* Du Pont system, page 403). The product is made cheap enough to enter the fertilizer market.

Urea contains more nitrogen (46.7 per cent) than is contained in any other fertilizer material. It is marketed as such as Uramon, containing 42 per cent urea-nitrogen, or more widely as a solution of crude urea in liquid ammonia, known as *urea-ammonia liquor* or more simply as *Ual.* This latter contains 15.1 per cent nitrogen as urea and 30.4 per cent nitrogen as ammonia, or a total of 45.5 per cent nitrogen. Urea reduces the vapor pressure of the ammonia and, since it is a neutral compound, more of this Ual can be added for ammoniation of a ton of superphosphate than is true of ammonia (200 lb. in comparison with 80 lb.).

Another important and growing application for crystal urea is in the plastics industry (Chap. XXXV) where, in combination with formaldehyde, it forms many useful products for the automobile, radio, hardware, and household industries. Urea is also finding employment in textiles (creaseproofing), in adhesives, in pharmaceuticals, and in the preparation of stains and finishes.

NITRIC ACID

Historical.—For many years nitric acid has been made from Chile saltpeter according to the following reaction:

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$

Some is still made by this procedure where the plants have not yet worn out or where there exists a particularly favorable locality with regard to the importation of crude sodium nitrate or Chile saltpeter. This process furnished niter cake, a very useful product, which for a long time was employed for the manufacture of hydrochloric acid by its reaction with salt. As a matter of fact, the niter cake was not $NaHSO_4$ which contains 40.8 per cent H_2SO_4, but a mixture of $NaHSO_4$ with some H_2SO_4 in order so to reduce the melting point that, for economical operation, the niter cake could be run out in a molten state.[2] The present, almost invariably more economical, process involves the commercialization of the oxidation reaction of ammonia with air or oxygen. This has become economical because of the decreasing price of ammonia and of the great savings of the plants in comparison with the old sodium nitrate procedure. Not only is the capital investment in the original plant less, but the maintenance expense and repair are greatly reduced.

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[1] THOMPSON, KRASE, and CLARK, Resistance of Metals to the System Urea-water-ammonium-carbonate, *Ind. Eng. Chem.*, **22**, 735 (1930).

[2] Fuller descriptions of this process are found in the older books where details are given of the equipment required and of the absorption procedures.

Uses and Economics.—Nitric acid has some direct application as an oxidizing acid in the parting of gold and silver, in the pickling of brass, and in photoengraving. However, its chief function is to make nitrates in both the inorganic and the organic fields as well as nitro derivatives in all branches of the organic division. The inorganic nitrates important commercially are those of ammonia, sodium, copper, and silver. Many of the nitrate or nitro compounds are used directly especially in the explosives industry as is true of ammonium nitrate, nitro-glycerine, and nitro-cellulose (really glyceryl trinitrate and cellulose polynitrate). Chloro-picrin, Cl_3CNO_2, is a very powerful and effective insecticide which is increasingly used in man's continual combat against depredating organisms. The nitro aromatic compounds, ammonium picrate, and T.N.T. as well as tetryl, are most important explosives. However, quite frequently the nitro group is used as an entering step into hydrocarbons of either aliphatic or aromatic divisions, in order to act as the stepping-stone to more technically useful derivatives. This is exemplified by nitro-benzene in the manufacture of aniline (*cf.* Chap. XXXVIII on intermediates and dyes) and the nitro-paraffins in leading to amines and amino-alcohols in the paraffin series (Chap. XXXIX). For these purposes, there is consumed in peacetimes approximately 110,000 to 165,000 tons of 100 per cent nitric acid annually (calculated from Table 6).

Commercial grades[1] of nitric acid are

36°Bé. or 1.330 sp. gr.	52.3 per cent HNO_3
40°Bé. or 1.381 sp. gr.	61.4 per cent HNO_3
42°Bé. or 1.408 sp. gr.	67.2 per cent HNO_3

Raw Materials.—The essential raw materials for the modern manufacture of nitric acid are anhydrous ammonia, air, and water. Because of the low molecular weight of the ammonia, it can be shipped economically from the large primary nitrogen-fixation plants to various oxidation plants at the consuming centers. This effects a great saving in freight as well as in equipment, because the anhydrous ammonia can be shipped in steel cars in comparison with shipping aqueous nitric acid in stainless-steel tank cars weighing five or six times the weight of the ammonia. To these basic raw materials should be added the stainless-steel alloys required for the nitric acid part of the oxidation plant. Such a chrome alloy has the composition:

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[1] PERRY, *op. cit.*, pp. 94, 419. The data given are for 60°F. (15.5°C.).

Carbon	0 10 per cent maximum
Chromium	17–20 per cent
Nickel	8–12 per cent
Columbium	10 times the carbon content

Reactions and Energy Changes.—The essential reactions for the production of nitric acid by the oxidation of ammonia may be represented as follows:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O(g); \quad \Delta H = -216{,}600 \text{ cal} \qquad (1)$$
$$2NO + O_2 \rightarrow 2NO_2; \quad \Delta H = -27{,}100 \text{ cal.} \qquad (2)$$
$$3NO_2 + H_2O(l) \rightarrow 2HNO_3(aq) + NO; \quad \Delta H = -32{,}200 \text{ cal.} \qquad (3)$$

There are several by-reactions which reduce somewhat the yield of reaction (1).

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O(g); \quad \Delta H = -302{,}700 \text{ cal.} \qquad (4)$$
$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O(g); \quad \Delta H = -431{,}900 \text{ cal.} \qquad (5)$$

Reaction (1) is essentially a very rapid catalytic one, carried on by passing about 10 per cent of ammonia by volume, mixed with air through the multilayered, silk fine, platinum gauze, at a temperature of approximately 750°C. (see Fig. 5). A great deal of work has been done on the study of the conditions surrounding these reactions, particularly by Andrussow.[1] This reaction is carried out either under atmospheric pressure or under about 100 lb. As can be seen from reaction (1), there is only a small increase in volume, so that the principle of Le Châtelier does not affect the equilibrium very substantially. Indeed Fauser in the International Nitrogen Conference, May, 1928, reported that an increase of 5 or 10 atm. had no noticeable effect upon the equilibrium. The increase in pressure, by compressing the reactants, enables a greater space velocity to be maintained with a consequent saving in plant until such a pressure is reached that the cost of the increased thickness of the stainless steel required more than counterbalances the saving in volume of the equipment per pound produced. Competent chemical engineers hold this to be at about 100 lb. This oxidation under pressure also furnishes a nitric acid containing 61 to 65 per cent HNO_3 in comparison with the 50 to 55 per cent HNO_3 obtained from atmospheric oxidation. The speed of the ammonia oxidation is extraordinarily high, giving an excellent conversion in the short contact time of 3×10^{-4} sec. upon passing through several layers of fine platinum gauze at 750°C. The conversion of this reaction is facilitated by employing an excess of air.

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[1] Andrussow, Catalytic Ammonia Oxidation, *Z. angew Chem*, **39**, 321–332 (1926); *cf* Chap. 14 by Krase in Curtis, *op. cit*, pp 366–408, *ff.*, for very full description of all factors pertaining to the basic physical chemistry surrounding the reactions, as well as the equipment necessary for its commercialization, together with copious references to the original literature.

Hence in the industrial procedure it has been found economical to mix initially with the ammonia all the air needed for reactions (1) and (2).

The oxidation of the nitric oxide, NO, to nitrogen dioxide, NO_2, is the slowest reaction, but the equilibrium is more favorable at lower temperatures. Hence this reaction is carried out in absorbers of considerable capacity and provided with cooling. Because of a decrease in volume, this reaction is favored under pressure according to the principle of Le Châtelier. While these factors raise the cost of the equipment for carrying out the oxidation of the nitric oxide, they increase the conversion. It is necessary in the design of a plant to know how long[1] this reaction will take, in order to calculate the volume needed for the equipment.

$$3NO_2 + H_2O \rightleftarrows 2HNO_3 + NO \qquad (3)$$

Equation (3) is really an absorption phenomenon. It is so considered in Perry[2] where various phases as developed by different investigators are presented, with formulas for calculating the capacity of towers to absorb NO_2 to form the HNO_3. This reaction, in the opinion of Taylor, Chilton, and Handforth,[3] is the controlling one in making nitric acid, and its rate was increased by employing an absorption tower under pressure and cooling, and with countercurrent graded strengths of acid for the absorption. Chemical engineers have developed a tower 5½ ft. in diameter and 40 ft. high with a capacity of over 25 tons of nitric acid per 24 hr. (*Cf.* Fig. 5.)

Manufacturing Procedures.—Commercialization of these oxidation reactions, from ammonia leading to nitric acid, are exemplified by the flow sheet given in Fig. 5, which depicts the present-day procedure under 100 lb. pressure. Small-scale plants without any absorption and final oxidation steps are employed to supply the nitric oxide needed as a catalyst[4] in the chamber sulfuric acid procedure. The energy changes involved in these reactions are given with the reactions themselves. Much of the power required for compressing the air to 100 lb. pressure can be regained by expanding the waste gas, mostly nitrogen, from the top of the absorption tower, through a compressor for part of the needed air. Naturally the drive cylinder of this power recovery compressor should be larger in diameter than the air cylinder. Actually per ton of 100 per cent nitric acid, the saving thus effected is 200 kw.-hr.

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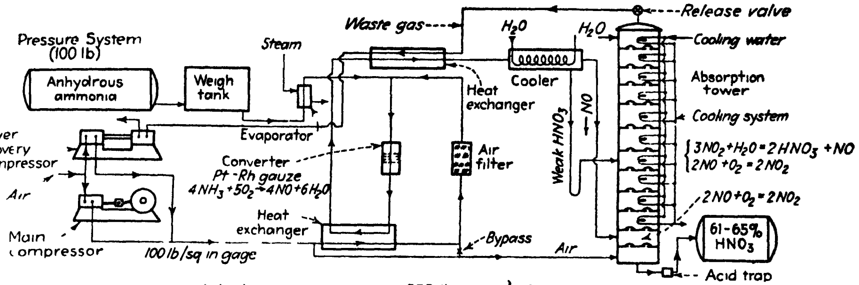
[1] KRASE, pp. 384*ff.* in Curtis, *op. cit.*, reviews the work of many researchers and presents equations and curves derived therefrom pertaining to the velocity of this reaction. For the calculation of time of this reaction as equaling 142 sec. at 25°C., see Krase in Curtis, *op. cit.*, p. 390.

[2] PERRY, *op. cit.*, pp. 1191–1195. The entire section on gas absorption should be studied.

[3] TAYLOR, CHILTON, and HANDFORTH, Manufacture of Nitric Acid by the Oxidation of Ammonia, *Ind. Eng. Chem.*, **23**, 860 (1931).

[4] SPANGLER, Ammonia Oxidation Replaces Niter for Chamber Acid Plants, *Chem. & Met. Eng.*, **35**, 342 (1928).



Anhydrous ammonia	575 lb	Per ton 100per cent HNO_3
Platinum*	Variable	
Power	>70 Kw-hr	
Direct labor	1 0 man-hr	

* In some plants, Pt loss is about 0 012 oz per ton

Reference on pressure synthesis Taylor, Chilton and Handforth Ind Eng Chem, Vol 23 p 860 (1931)

FIG. 5.—Synthetic nitric acid (100 lb. pressure).

Unit Operations and Unit Processes.—Figure 5 can be separated into the following coordinated sequences:

Anhydrous ammonia is evaporated continuously and uniformly in an evaporator, using steam to supply the necessary heat of evaporation (Op.). Air for all reactions shown on Fig. 5 is compressed in power recovery compressor and in motor-driven compressor to 100 lb. and passed through heat exchangers and air filter (Op.).

Ammonia gas is oxidized with air to nitric oxide at 100 lb. pressure in a converter, by passing through a platinum gauze at 750°C. (Pr.).

Then nitric oxide with the excess air necessary for the succeeding oxidizing steps is cooled in two heat exchangers and a water cooler, and conducted to the bottom of the absorption tower (Op.).

The successive oxidations and hydrations of the nitric oxide are carried out with continuous water cooling in a stainless-steel absorption tower (Pr. and Op.).

The nitric acid (61 to 65 per cent HNO_3) is drawn off through a gas or acid trap (Op.).

The waste gas from the top of the absorption tower is heated in an exchanger counter to reaction gases and expanded through a compressor for part of the air, before being exhausted to the atmosphere (Op.).

Concentration of Nitric Acid.—The usual way to obtain the stronger nitric acid (95 or 98 per cent) needed generally by industry, from the 61 to 65 per cent acid yielded by the ammonia oxidation and absorption at 100 lb. pressure, is to take advantage of the dehydrating action of sulfuric acid to destroy the constant-boiling mixture of water and 68 per cent nitric acid. Either in a pot still or in a continuous pipe still, the weaker nitric is mixed with sulfuric acid, usually 64 to 66°Bé., and the

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[1] SILLICK, Concentrated Nitric Acid by Fractionation of the Mixture: Nitric Acid-Water-Sulfuric Acid, *Ind. Eng. Chem.*, **33**, 1248 (1941).

strong nitric distilled[1] off and condensed. The strength of the distillate depends on the concentration of the sulfuric acid and its temperature. The nitric acid condenser is made either of stainless steel or Duriron. Such strong nitric acid is very frequently mixed with sulfuric acid or oleum to make mixed acid for nitrations. The partly diluted (75 per cent) sulfuric acid is reconcentrated and reused (*cf.* Chap. XIX). If the ammonia is oxidized and absorbed at atmospheric pressure, the resulting nitric acid is only 55 per cent strong, and hence presents a more costly concentration step than if a stronger acid were obtained.

SODIUM NITRATE

In recent years large tonnages of sodium nitrate[1] have been made both in America at Hopewell and in Europe by reaction of sodium chloride and soda ash from ammonia-soda or Solvay process, with nitric acid from ammonia oxidation. This is a high-grade product and is sought after for both industrial and fertilizer demands. Such sodium nitrate is particularly excellent in the making of dynamite.

The Chilean nitrate industry was, until the rise of the synthetic ammonia industry, the dominating factor in the world's nitrogen supply. The 50-year-old Shanks process for obtaining the nitrate was inefficient and could not meet the competition. So following the First World War, lean years came to Chile, which had depended on the export tax upon its nitrate for its financial mainstay (42.8 per cent of total revenue or over 1 billion dollars from 1880 to 1930). Also 10 per cent of the total population of Chile had been directly connected with this industry.

These Chilean deposits occur in a desert area at an elevation of from 4,000 to 9,000 ft. and extending some 400 miles north and south with a width of from 5 to 40 miles. The crude salt deposit is called *caliche* and has the following typical analysis, according to Curtis:

	Per cent		Per cent
Sodium nitrate	17.6	Magnesium sulfate	3.9
Potassium nitrate	1.3	Calcium sulfate	5.5
Sodium chloride	16.1	Sodium iodate	0.11
Sodium sulfate	6.5	Sodium borate	0.94
Potassium perchlorate	0.23		

The *caliche* usually worked varies in thickness from 8 in. to 14 ft. with an overburden of from 1 to 4 ft. There are still enormous deposits available.

In 1920 the Guggenheim Brothers of New York, owners and developers of large copper-mining operations, started to study the obtaining of sodium nitrate from *caliche*. By applying modern chemical-engineering knowledge of the *unit operations* of mining, transportation, crushing, selective leaching, crystallization, and heat transfer, the Guggenheim process has resulted. This has been applied (1) in the Oficina Maria Elena, which produces 520,000 metric tons of sodium nitrate per year and cost $43,000,000, and (2) in the Pedro de Valdivia plant, which produces 750,000 tons of finished nitrate per year and cost $32,000,000.

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[1] CURTIS, *op. cit.*, pp. 54–70, 415–416; "Chemical Nitrogen," *op. cit.*, pp. 107–122.

The Guggenheim process as perfected consists of improved leaching and crystallization operations on a very large scale using modern labor-saving machinery and various heatsaving devices. The leaching is countercurrent at 40°C. with crystallization down to 5°C. The heat required for the 40°C. level is from heat exchangers in connection with the ammonia condensers and from the exhaust gases and cooling water from the large Diesel engines which supply the plant with electric power. The 5°C. level is attained (1) to 15°C. in heat interchangers counter to the nitrate mother liquor and (2) to 5°C. by ammonia refrigeration. This results in an increased production[1] of from 25 to 30 tons of nitrate from a ton of fuel for the Guggenheim process in comparison with 6 to 7 tons by the Shanks process. The Chilean nitrate industry produces as *ly-products* the world's main supply of iodine and also substantial quantities of potassium nitrate.

Problem

Where the presence of nitrogen is not objectionable, hydrogen for reductions may be produced by cracking ammonia at high temperature. A cylinder of hydrogen under high pressure contains 1 lb. of hydrogen and weighs approximately 100 lb. An ammonia cylinder containing 100 lb. of ammonia weighs approximately 150 lb. A plant wishes to reduce 1 ton of Fe_2O_3 to metallic iron per day with hydrogen. If freight is 20 cents per 100 lb. hauled and it costs 3 cents per pound to crack ammonia, calculate and compare the costs of cylinder hydrogen and hydrogen from ammonia. Ammonia costs 12 cents per pound and cylinder hydrogen $1 per pound.

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[1] "Chemical Nitrogen," *op. cit.*, p. 112. For numerous flow sheets covering the Guggenheim process see Curtis, *op. cit.*, pp. 64–67.

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CHAPTER XXI

HYDROCHLORIC ACID AND MISCELLANEOUS INORGANIC CHEMICALS

The manufacture of many inorganic chemicals has been subjected to much new study in the past few years, with the result that new processes are in use for old chemicals or that improvements have been made in old processes. An example of a new process is the recovery of bromine from sea water, and of an improvement is the employment of structural carbon to build hydrochloric acid plants.

HYDROCHLORIC OR MURIATIC ACID

Hydrochloric acid, although not manufactured in such large quantities as sulfuric acid, is an important heavy chemical. Manufacturing techniques have changed and improved in recent years and new procedures are employed such as the burning of chlorine in hydrogen.

Hydrogen chloride, HCl, is a gas at ordinary temperatures and pressures. Aqueous solutions of it are known as *hydrochloric acid* or, if the hydrogen chloride in solution is of the commercial grade, as *muriatic acid.* The common acids of commerce are 18°Bé. (1.142 sp. gr.) or 27.9 per cent HCl, 20°Bé. (1.160 sp. gr.) or 32.0 per cent HCl, and 22°Bé. (1.179 sp. gr.) or 35.8 per cent HCl.[1] Anhydrous hydrogen chloride is available in steel cylinders at a very considerable increase in cost, owing to the cylinder expense involved.

Historical.—Hydrogen chloride was discovered in the fifteenth century by Basilius Valentinius. Commercial production of hydrochloric acid began in England when legislation was passed prohibiting the indiscriminate discharge of hydrogen chloride into the atmosphere. This legislation forced manufacturers, using the LeBlanc process for soda ash, to absorb the waste hydrogen chloride in water. As more uses for hydrochloric acid were discovered, plants were built solely for its production.[2]

Uses and Economics.—Hydrochloric acid is employed in the manufacture of many of its salts. The bone-glue industry is a consumer of this acid, and its application as a reactivator of bone charcoal is important. It is used for etching and cleaning metal surfaces. Hydrochloric acid is consumed in the dye industry in diazotization and manufacture of aniline salt. Small amounts are necessary as a catalyst for the reduction of nitro groups. It is used in many organic syntheses such as of vinyl chloride from acetylene, of chloroprene from vinyl-acetylene, and the production of camphor from pinene. Anhydrous hydrogen chloride is reacted with ethylene to produce ethyl chloride as a step in the manufacture of tetraethyl lead. The Bergius wood hydrolysis process, which has never become commercial in the United States, employs hydrochloric acid of 40 per cent concentration. Small amounts of hydrochloric acid catalyze the hydrolysis of corn starch to corn sirup and sugar. The Dowell process for the rejuvenation[1] of old petroleum wells is a large consumer of muriatic acid.

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[1] PERRY, *op. cit.*, pp. 93 and 417; "The Condensed Chemical Dictionary," p. 71, 3d ed., Reinhold Publishing Corporation, New York, 1942.

[2] ULLMANN, "Enzyklopaedie der technischen Chemie," vol. 9, pp. 52–72, Urban and Schwarzenberg, Berlin and Vienna, 1932.

Manufacture.—The manufacture of hydrochloric acid may be considered to consist of three steps: (1) generation of hydrogen chloride, (2) purification, (3) absorption in water.[2] Several sources are available for the generation of hydrogen chloride but the most important are the action of sulfuric acid (or niter cake) on common salt, the combustion of chlorine in hydrogen[3] (synthetic process), and the by-product in the chlorination of both aromatic and aliphatic hydrocarbons.

Reactions and Energy Requirements.—The reactions of the salt-sulfuric acid process are endothermic.

$$NaCl + H_2SO_4 \rightarrow HCl + NaHSO_4 \qquad (1)$$

$$NaCl + NaHSO_4 \rightarrow HCl + Na_2SO_4 \qquad (2)$$

Summation:

$$2NaCl(s) + H_2SO_4(l) \rightarrow 2HCl(g) + Na_2SO_4(s); \qquad \Delta H = +15{,}800 \text{ cal.}$$

The first reaction goes to completion at relatively low temperatures while the second approaches completion only at elevated temperatures. The reactions are forced to the right by the escape of the hydrogen chloride from the reaction mass. The reaction between hydrogen and chlorine is highly exothermic and goes spontaneously to completion as soon as it is initiated.

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) \rightarrow HCl(g); \qquad \Delta H = -22{,}000 \text{ cal.}$$

The chlorination of aliphatic and aromatic hydrocarbons evolves large amounts of heat, making necessary the use of jacketed equipment for control of the temperature of reaction.[1] A typical chlorination may be formulated as follows:

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[1] Dow Chemical Company, Midland, Mich.

[2] PERRY *op. cit.*, pp. 1190*ff.*, especially pp. 1196–1199 for equipment. Chapter V, pp. 111–117 with references on p. 133 of Badger and Baker, "Inorganic Chemical Technology," is particularly good in presenting diagrams of furnaces and conditions for absorption; 2d ed. McGraw-Hill Book Company, Inc., New York, 1941.

[3] MAUDE, Anhydrous Hydrogen Chloride Gas, *Trans. Am. Inst. Chem. Engrs.*, **38**, 865 (1942).

$$\underset{\text{Benzene}}{C_6H_6} + Cl_2 \rightarrow \underset{\text{Chloro-benzene}}{C_6H_5Cl} + HCl$$

The absorption of the HCl, made by any process, liberates around 700 B.t.u. per lb. of HCl absorbed. This heat must be taken away in the absorber or the efficiency will be low.

Figure 1 illustrates the essential steps in the production of hydrochloric acid using the salt process and the synthetic process. The by-product process differs from these in the variable conditions employed for the production and separation of the hydrogen chloride. The *salt process* may be divided into the following *unit operations* (Op.) and *unit processes* (Pr.):

TABLE 1.—PRODUCTION OF HYDROCHLORIC ACID[a]
(In short tons, 100 per cent acid)

Source	1937	1939	1942	1943
Salt	53,000	53,000		
Chlorine	10,000	10,000		
By-product	8,000	16,000		
Total	71,000	79,000	297,099	331,365

[a] *Chem. & Met. Eng.*, **51**, No. 2, 130 (1944); BADGER and BAKER, "Inorganic Chemical Technology," 2d ed., McGraw-Hill Book Company, Inc., New York, 1941. Most of the hydrochloric acid entering commerce is sold with about 2 parts of water.

Sulfuric acid (or niter cake if available) and salt are roasted in a furnace to form hydrogen chloride and sodium sulfate (salt cake) (Pr.).

The hot hydrogen chloride, contaminated with droplets of sulfuric acid and particles of salt cake, is cooled by passing it through a series of S-shaped silica coolers, cooled externally by water (Op.).

The cooled gas is then passed upward through a coke tower to remove suspended foreign materials (Op.). (This equipment is omitted in some plants.)

Purified hydrogen chloride from the top of the coke tower is absorbed in water in a silica absorber (Op.).

Finished hydrochloric acid is withdrawn from the bottom of the absorber, and any undissolved gas passing out the top of the absorber is scrubbed out with water in a packed tower (Op.).

The most important of the salt furnaces in operation is the Mannheim furnace. This consists of a cast-iron muffle, composed of a dish-shaped top and bottom bolted together and equipped with plows to agitate the reaction mixture. The furnace is calked with asbestos rope. Heat is supplied around the entire furnace by combustion gases from a coal fire.

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[1] GROGGINS, "Unit Processes in Organic Synthesis," pp. 153–232, McGraw-Hill Book Company, Inc., New York, 1938.

The *synthetic process* generates hydrogen chloride by burning chlorine in a few per cent excess of hydrogen. The purity of the ensuing acid is dependent upon the purity of the hydrogen and chlorine. However, as both of these gases are available in a very pure state as by-products of the electrolytic process for caustic soda, this synthetic method produces the purest hydrogen chloride of all the processes. The cooling and absorption are very similar to that employed in the salt process.

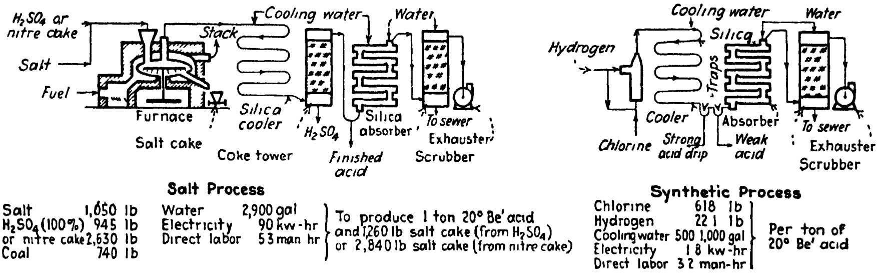

FIG. 1.—Flow sheet for hydrochloric acid.

Hydrochloric acid is also made from chlorine by burning it in methane with a regulated amount of air.

$$2Cl_2 + CH_4 + \text{air} \rightarrow 4HCl + CO_2$$

Hydrochloric acid is extremely corrosive to most of the common metals and great care should be taken to choose the proper materials for the plant construction.[1] This acid is usually shipped and stored in rubber-lined steel tanks. As mentioned previously, the absorbers and condensers are frequently made of silica, but in very recent years tantalum and structural carbon have somewhat replaced fused silica. Indeed, the installation of Karbate carbon structural heat interchangers and condensers has characterized the recent hydrochloric acid plants. These have the advantages of being nonfragile and of having excellent heat-transfer coefficients.[2]

BROMINE

Bromine is a member of the halogen family and is a heavy dark-brown liquid. It is much less common and more expensive than chlorine.

Historical.—In 1826, 15 years after the discovery of iodine, bromine was discovered by Balard, a French chemist, who obtained it from the mother liquor left after separating the salt from evaporated sea water.

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[1] PERRY, *op. cit.*, p. 2100, gives tabulated materials to withstand hydrochloric acid.

[2] HUNTER, Absorption of Hydrogen Chloride, *Trans. Am. Inst. Chem. Engrs.*, **37**, 741 (1941). See Chap. IX on Industrial Carbon

Its manufacture from the Stassfurt deposits of carnallite was begun in 1865, the bromine having accumulated as $MgBr_2$ in the liquors left after working up $MgCl_2$ and KCl. Production amounted to 2,500 lb. the first year.[1] America's earliest (1895) successful bromine plant operated on salt brines. In 1925 the Ethyl Gasoline Corporation sponsored the experimental operation of a floating chemical factory, designed to remove the bromine from sea water as tribromoaniline. At about this time the Dow Chemical Company also became interested in "sea-water bromine." After many years of preliminary research a plant using the Ethyl-Dow process was erected at Kure Beach, N.C. Production was begun in 1934. The plant was later expanded, so that a 10,000-ton annual output was possible. A newer plant has been erected at Freeport, Tex.[2]

Uses and Economics.—Bromine is employed in chemical analysis. Bromocyanogen is prepared from it for use in the treatment of gold telluride ores. The greatest single use for the liquid, however, is in the manufacture of ethylene bromide for antiknock gasoline to prevent deposition of lead in the gasoline motor. Its second largest use is in the preparation of alkali bromides, which are widely consumed as a comparatively safe sedative in medicine. These bromides also are essential constituents in the field of photography. In addition to the above, bromine is employed in the preparation of dyes, disinfectants, war gases, and the refining of platinum.[3]

Prior to the First World War, Germany supplied approximately three quarters of the total world production of bromine, which amounted to some 1,250 tons. By 1924, the United States alone was producing 1,017 tons and importing 612 tons.[4] By 1929, the total domestic production had risen to 3,207 tons; in 1938, it had reached 16,162 tons and in 1940, about 25,000 tons. Imports, on the other hand, fell off steadily from 8½ tons in 1929 to none at all in 1938.[5]

The price of bromine has varied greatly from 10 cents per pound in 1908 to $1.31 per pound in 1916. Since the First World War, however, it has been somewhat stabilized, being 17 cents in 1923, 27 cents in 1929, and from 20 to 30 cents per pound since 1938. The major part of the bromine is shipped as ethylene dibromide.

Manufacture.—Bromine is manufactured in a variety of ways. In the United States the chief raw material is sea water in which it occurs in concentrations of 60 to 70 p.p.m. It is also manufactured from natural brines, where its concentration may be as high as 1,300 p.p.m. In Germany it is produced from waste liquors resulting from the extraction of potash salts from the carnallite deposits of Stassfurt, which were formerly the chief source of bromine in the world. Various other countries have the following sources of bromine: Italy extracts it from one of the largest inland lakes of the country; Russia from the water of Saksky Lake in the Crimea district; France from deposits in Alsace and, if necessary, from the inland salt lakes of Tunis.

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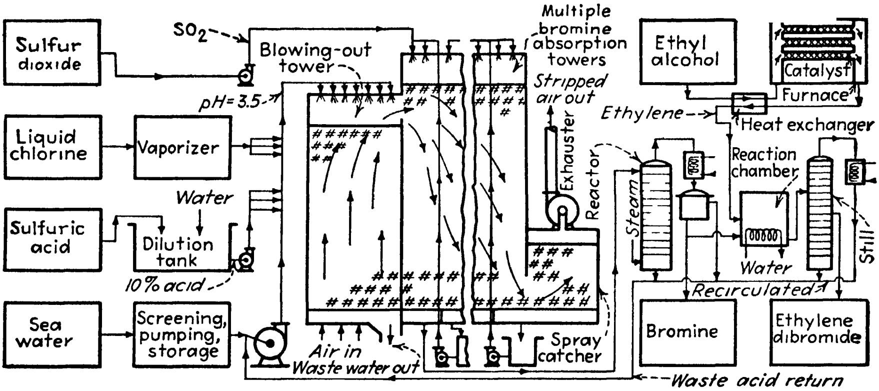
[1] DYSON, Industrial Aspects of Bromine and Its Compounds, *Chem. Age*, **23**, 425, 425, 450 (1930).

[2] "Bureau of Mines Mineral Yearbook for 1938," p. 1269, U.S. Department of the Interior, Washington.

[3] DYSON, *op. cit.*

[4] LONG, The Future Demand for Bromine, *Ind. Eng. Chem.*, **18**, 425 (1926).

[5] Facts and Figures of the American Chemical Industry, 1939–1940, Washington, D.C.; *Chem. & Met. Eng.*, **46**, 509, (1939).



Reactions: $Br_2 + SO_2 + 2H_2O \rightarrow 2HBr + H_2SO_4$; $2HBr + Cl_2 \rightarrow 2HCl + Br_2$

FIG. 2.—Flow sheet for bromine from sea water.

Bromine from Sea Water.—Sea water contains 65 to 70 p.p.m. bromine in the form of bromide ions, in addition to its other constituents, as shown by sea-water analysis in Chap. XI. A process was worked out for the removal of this small quantity of bromine by adding aniline to chlorinated sea water, according to the equation:

$$3NaBr + 3Cl_2 + C_6H_5NH_2 \rightarrow C_6H_2NH_2Br_3 + 3NaCl + 3HCl$$

The process was operated on board a floating chemical factory, the *S.S. Ethyl.* The Dow Chemical Company succeeded in devising a more economical process, without the use of aniline. By this process, the bromide-containing brine is (1) oxidized with chlorine, (2) blown with air to free bromine, and (3) the bromine is reacted with sulfur dioxide and absorbed. The process has been made a commercial success by the Ethyl-Dow Corporation which now has two operating plants. This "blowing-out" process functions according to the flow sheet of Fig. 2 which can be broken down into the following coordinated sequences[1] of *unit operations* (Op.) and *unit processes* (Pr.):

---

[1] See also, pictured flow sheet, *Chem. & Met. Eng.*, **46**, 771 (1939). Old soda ash absorption is described.

Sea water is allowed to flow into a settling basin, thence over a traveling screen and into a pond, from which it is pumped into the extraction plant (Op.).

The water from the pond is sent into a 42-in. rubber-lined pipe where acid from the end of the process, supplemented by a dilute sulfuric acid, is added to reduce the pH to 3 and to suppress subsequent reaction of the chlorine (Pr.).

The sea water is pumped to the top of the blowing-out tower after having had chlorine added through a rubber-lined pipe (Op. and Pr.).

$$2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$$

Air, sucked up through the wood-packed tower by powerful fans, blows out the freed bromine from the sea water which is returned to the sea (Op.).

The moist bromine-containing air is mixed with sulfur dioxide and conducted to an adjacent absorption tower where fans draw it through downcoming water or circulating solution.

$$Br_2 + SO_2 + 2H_2O \rightarrow 2HBr + H_2SO_4$$

The tower may be divided into multiple chambers connected in series. The water or recirculated solution enters through nozzles at the top and flows down through the chamber into a receiving tank, from which it is recirculated until a strong bromine-hydrobromic acid solution is obtained (Op. and Pr.).

Bromine dissolves in hydrobromic acid solution. This strong solution is pumped to storage (Op.).

After the bromine-hydrobromic acid solution has been collected, it is reacted with chlorine, the free bromine vapors are steamed out of solution and collected in liquid form (Op. and Pr.).

It is then used to manufacture ethylene dibromide through reactions with ethylene, prepared from ethyl alcohol (Pr.)

The residual acid, $H_2SO_4 + HCl$, solution is pumped to the start of the process to reduce the pH of the entering sea water (Op. and Pr.) Over-all plant efficiency is 90 per cent plus.[1]

Manufacture from Salt Brines.—Salt brines containing bromides are reacted with chlorine in the presence of sulfuric acid, steam being used to remove the liberated bromine. The steam-bromine mixture is condensed in stoneware condensers. A lower layer of dark-red bromine and an upper bromine-water layer separate. The bromine in the latter is recovered by blowing with air, passing the mixture through a tower filled with wet iron filings, and collecting the resulting ferrous bromide. This is treated with chlorine gas, liberating the bromine. In Germany, the solution (brine) containing 6 per cent bromine from action of chlorine upon bromides is warmed to 60°C. and allowed to trickle down a tower against rising steam which drives off 90 per cent of the bromine. The vapor is condensed in silica coils by ice water, and the residual gas sent to a tower filled with iron turnings.[1]

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[1] STEWART, Commercial Extraction of Bromine from Sea Water, *Ind. Eng. Chem.*, **26**, 361 (1934). This describes the old and less efficient soda ash absorption. See HEATH, U.S. Pat. 2143223 (Jan. 10, 1939), and HOOKER, U.S. Pat., 2143224 (Jan. 10, 1939) for modern modifications included above.

Crude bromine from any of the foregoing processes can be purified by redistillation or by passing the vapors over iron filings which hold back the chlorine impurity. The alkali bromides account for an important proportion of the bromine produced. They cannot be made by the action of caustic soda on bromine, since hypobromites and bromates are produced also. The approved method consists in allowing bromine to trickle into a mixture of water and iron borings until a heavy sirup of ferrous bromide has formed. This is siphoned off, treated with the desired alkali carbonate, filtered to remove the precipitate of iron hydroxides, evaporated, and recrystallized.

IODINE

Historical and Raw Materials.—It was in 1811 that M. Courtois, a saltpeter manufacturer of Paris, obtained a beautiful violet vapor from the mother liquors left from the recrystallization of certain salts. This iodine was later found to exist almost universally in nature. It is present as iodates (0.05 to 0.15 per cent) in the Chilean nitrate deposits. It occurs in sea water from which certain seaweeds extract and concentrate it within their cells. The iodine has been made from these weeds by the kelp-burning process which has been practiced for years in Scotland, Norway, and Normandy.[2] The present sources of the element, as far as the United States is concerned, however, are the nitrate fields of Chile and the oil-well brines of California.

Uses and Economics.—Iodine is used as a catalyst for the chlorination of organic compounds and in analytical chemistry for the determination of so-called *iodine numbers* of oils. The iodine for medicinal, photographic, and pharmaceutical purposes is usually in the form of alkali iodides, prepared through the agency of ferroso-ferric iodide. In addition to the above, the element is also employed for the manufacture of certain dyes and as a germicide. The simple iodine derivatives of the hydrocarbons, such as iodoform, have antiseptic action. The United States is at present producing from ½ to 1 ton of iodine per day, which amounts to about a quarter to a third of its annual consumption; the remainder is imported. For years, Chilean-produced iodine dominated the market and controlled the price which was set at $4.65 per pound. World production was about 1,000 tons, 70 per cent from Chile. Upon development of the iodine from the oil-well brines of the Southwestern United States, a potential domestic production of 500 tons annually became available. In recognition of this source, the price of iodine was reduced to approximately \$3.50 per pound in 1932. A year later domestic production had risen to 200 tons per year, a little over 22 per cent of our annual consumption. Import prices declined steadily, reaching 90 cents in 1935. In 1937 the price had reached 81 cents per pound. Since then, it has risen somewhat. Table 2 presents the iodine importations for the years 1936–1940.

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[1] Dyson, *op. cit.*

[2] Dyson, Chemistry and Chemotherapy of Iodine and Its Derivatives, *Chem. Age*, **22**, 362 (1930).

TABLE 2.—CRUDE IODINE IMPORTED FOR CONSUMPTION IN THE UNITED STATES, 1936–1940[a]

Year	Pounds	Value
1936	592,217	\$558,326
1937	1,967,148	1,784,491
1938	570,532	464,303
1939	200,000	168,238
1940	1,244,146	1,296,181

[a] HESSEL, MURPHY, and HESSEL, "Strategic Materials in Hemisphere Defense," p. 127, Hastings House, New York, 1942.

Manufacture.—The major sources for the production of industrial iodine are from Chilean nitrate mother liquor and from oil-well brines of California. The Chilean process is the more important from the standpoint of world production.

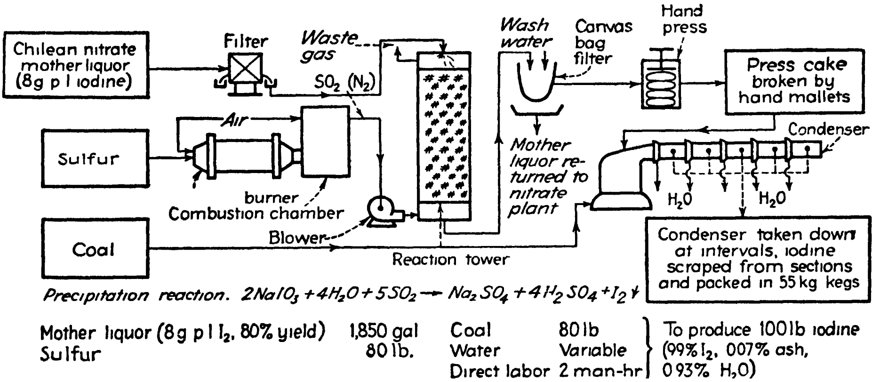
Chilean nitrate mother liquor (8g p l iodine)
Filter
Waste gas
SO_2 (N_2)
Sulfur
Air
burner
Combustion chamber
Blower
Coal
Reaction tower
Wash water
Canvas bag filter
Hand press
Press cake broken by hand mallets
Condenser
Mother liquor returned to nitrate plant
H_2O
H_2O
Condenser taken down at intervals, iodine scraped from sections and packed in 55 kg kegs
Precipitation reaction. $2NaIO_3 + 4H_2O + 5SO_2 \rightarrow Na_2SO_4 + 4H_2SO_4 + I_2\downarrow$
Mother liquor (8g p l I_2, 80% yield) 1,850 gal
Sulfur 80 lb.
Coal 80 lb
Water Variable
Direct labor 2 man-hr
To produce 100 lb iodine (99% I_2, 0.07% ash, 0.93% H_2O)

FIG. 3.—Iodine from Chilean nitrate mother liquor.

Chilean Iodine.—Figure 3 shows the essential steps in the production of Chilean iodine. The initial concentration of iodine, usually as iodate, in the nitrate liquor is 6 to 12 g. per l. The liquor runs down a tower and meets a stream of ascending sulfur dioxide which liberates the iodine according to the reaction:[1]

$$2NaIO_3 + 4H_2O + 5SO_2 \rightarrow Na_2SO_4 + 4H_2SO_4 + I_2$$

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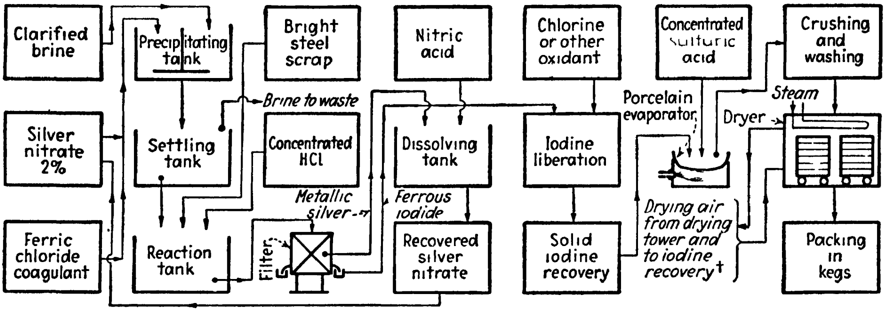
[1] HOLSTEIN, Fortunes and Misfortunes in Iodine, *Chem. & Met. Eng.*, **39**, 422 (1932); FAUST, The Production of Iodine in Chile, *Ind. Eng. Chem.*, **18**, 808 (1926).

The iodine is filtered in canvas bags, which are pressed to remove water. The resulting cake, containing approximately 80 per cent iodine, is put into cement-lined retorts and sublimed. The vapors are condensed in earthenware pipes 2 ft. in diameter by 4 ft. long, jointed with mud and jute. The water present in the vapor condenses and runs down the granules of iodine which collect on the sides. The iodine is packed in kegs covered with fresh cowhide and is 99 to 99.5 per cent pure. The average over-all yield from mother liquor is 70 per cent, which represents an extraction of only 25 to 30 per cent of the iodine present in the original raw material.



Certain details of process are not available and cannot be shown on this flow sheet

† Air dried over $CaCl_2$, vaporized iodine recovered in tower irrigated with alkali solution

FIG. 4.—Iodine from oil brines by the silver iodide process.

In addition to the foregoing process, iodine was also made (1) by reduction with sodium thiosulfate and sulfuric acid and (2) by the reaction of sodium bisulfite either prepared at the plant by reacting soda ash with sulfur dioxide or imported.

American Iodine (from oil brines).—Certain California oil wells are producing by-product brines containing 30 to 70 p.p.m. iodide ion. The extraction of this iodine has been attempted by various processes: (1) extraction with kerosene, (2) silver iodide process, (3) activated carbon process, (4) Turrentine process, (5) precipitation by cuprous and mercurous salts, (6) blowing out by air after chlorinating. Only the second and sixth are of present-day importance.[1] The brine is first cleaned and freed of oil and dirt in sand filters operating in series. The iodine may then be recovered by the *silver iodide process* as depicted in Fig. 4. The iodine is precipitated by treatment with a 2 per cent silver nitrate solution, in the presence of ferric chloride solution as a coagulant. A wooden tub is used. The mixed $AgI\text{-}Fe(OH)_3$ precipitate settles and is treated with concentrated hydrochloric acid to dissolve the iron precipitate. Steel scrap is added, forming ferrous iodide and silver metal, the reaction being completed within about an hour. The silver is filtered and reoxidized to silver nitrate, while the ferrous iodide solution is treated with an oxidant, Cl_2, HNO_3 or $Na_2Cr_2O_7$ and H_2SO_4, to precipitate the iodine. This iodine is melted under concentrated sulfuric acid and the purified iodine taken off. The resulting cake is washed and dried in a special drying chamber. It is not sublimed but is shipped in 200-lb. kegs as a 99.8 per cent pure product.

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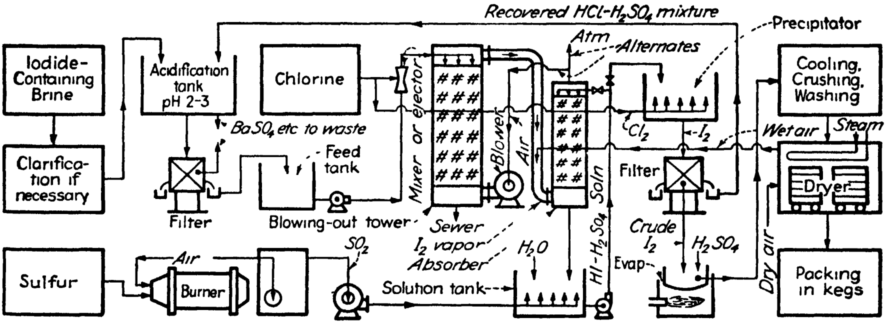
[1] ROBERTSON, New American Iodine Industry, *Ind. Eng. Chem.*, **26**, 376 (1934), supplemented by *private communications*.

The *activated carbon process* has been abandoned for a number of years as uneconomical. Clarified brine was acidified with sulfuric acid and treated with sodium nitrite in a large. tank, the reaction being as follows:

$$NaI + H_2SO_4 + NaNO_2 \rightarrow Na_2SO_4 + \tfrac{1}{2}I_2 + NO + H_2O$$

The free iodine produced colored the solution yellow. This solution was treated with activated carbon in 300,000-gal. adsorption tanks, the carbon adsorbing the iodine, and the aqueous liquor was wasted. The carbon was reused until loaded with iodine, when it was filtered on a canvas-bottomed filter. The iodine was extracted with hot caustic soda in an agitated tank, producing NaI and $NaIO_3$, and the suspended carbon was filtered and reused. The approximately 3 per cent iodide-iodate solution was concentrated, cooled, and chlorinated in a pot still. The iodine was sublimed out and condensed in a ceramic condenser. This crude granular mass was purified by melting under sulfuric acid, cooled, crushed, and washed. The wet iodine was collected, dried on trays in a heated room through which was circulated air dried with calcium chloride, the air being washed with alkali to remove any iodine.



Reactions $\begin{cases} 2\,MI + Cl_2 \rightarrow 2\,MCl_2 + I_2\uparrow;\ I_2 + SO_2 + 2H_2O \rightarrow 2\,HI + H_2SO_4 \\ I_2 \text{ vapor dissolves in HI soln};\ 2\,HI\,(+H_2SO_4) + Cl_2 \rightarrow 2\,HCl\,(+H_2SO_4) + I_2\downarrow \end{cases}$

FIG. 5.—Iodine from oil brines (SO_2 absorption process).

The present active producer[1] at Seal Beach, near Long Beach, Calif., frees the iodine in the acidified oil-well brine by chlorine and *blows out* the

[1] HEATH, U.S. Pat., 2143222 (Jan. 10, 1939); HOOKER, U.S. Pat., 2143224 (Jan. 10, 1939). See Bromine, p. 420.

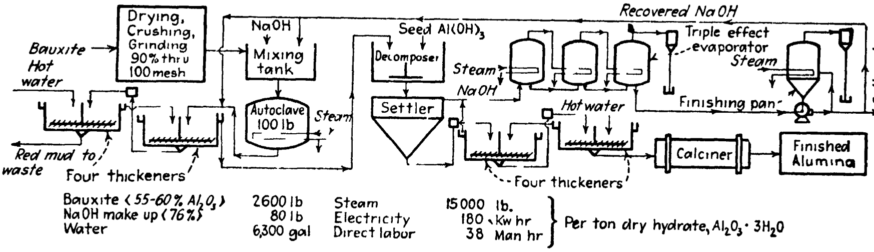
iodine with air. The iodine is reacted with sulfur dioxide and absorbed, liberated, filtered, and dried. The reactions are

$$\begin{aligned} 2NaI + Cl_2 &\rightarrow 2NaCl + I_2 \text{ (vapor)} \\ I_2 + SO_2 + 2H_2O &\rightarrow 2HI + H_2SO_4 \\ 2HI + Cl_2 &\rightarrow 2HCl + I_2 \text{ (mostly solid)} \end{aligned}$$

The absorption of the HI is in water or in a solution containing HI, circulated to increase the concentration. The iodine upon liberation from the strong solution by chlorine is filtered off. The mother liquor, containing a small amount of iodine and the sulfuric and hydrochloric acids formed by the reactions, is sent to the start of the process to acidify the brine (see Fig. 5)

ALUMINA

Alumina, Al_2O_3, is such an important chemical because it is the raw material for metallic aluminum (*cf.* Chap. XVI).



Bauxite (55-60% Al_2O_3)	2600 lb	Steam	15000 lb.	Per ton dry hydrate, $Al_2O_3 \cdot 3H_2O$
NaOH make up (76%)	80 lb	Electricity	180 Kw hr	
Water	6,300 gal	Direct labor	38 Man hr	

FIG. 6.—Alumina by Bayer process (filter usually interposed between last thickener and calciner).

Uses and Economics.—Large quantities of alumina are produced yearly for the manufacture of metallic aluminum. It has been estimated that, in 1943, over 4 billion pounds of alumina were produced for conversion to metal.[1] In addition, a large amount (52,413 short tons[2] in 1942) is also manufactured into activated alumina, abrasives, and other miscellaneous products.

Manufacture.—Figure 6 shows the essential steps in the production of alumina from bauxite by the Bayer process.[3] The steps involved may be divided into the following *unit operations* (Op.) and *unit processes* (Pr.):

Bauxite, a mineral containing about 55 per cent aluminum oxide and less than 7 per cent silica, is dried, crushed, and ground to 100 mesh (Op.).

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[1] JOLLY, The Recent Expansion of the Aluminum Industry, *Science*, **96**, No. 2480, 29 (1942).

[2] Mineral Industry Surveys, *U.S. Bur. Mines* M.M.S. 1048, Apr. 27, 1943.

[3] See also the pictured flow sheets, *Chem. & Met. Eng.*, **47**, 707 (1940); *Chem. & Met. Eng.*, **50**, No. 4, 145–150, 154–157 (1943); LEE, Making Alumina at Mobile, *Chem. & Met. Eng.*, **47**, 674 (1940).

The finely divided bauxite is dissolved under pressure in a hot, concentrated caustic soda solution (Pr.). Sodium aluminate is formed and the dissolved silica is precipitated as sodium aluminum silicate.

The undissolved residue (red mud) is separated from the alumina solution by filtration and washing and sent to recovery (Op.). Kelly or Oliver filters are used.

The solution of sodium aluminate is hydrolyzed to aluminum hydroxide by cooling and by dilution with wash waters; the aluminum hydroxide is induced to crystallize by seeding (Op. and Pr.).

The precipitate is separated from the liquor and clarified in tray thickeners and then washed with hot water. It is filtered in Dorrco or Vallez filters (Op.).

The aluminum hydroxide is calcined up to 1800°C. to alumina in a rotary kiln (Pr.).

The alumina is cooled and shipped to the reduction plants (Op.).

The dilute caustic soda filtered from the aluminum hydroxide is concentrated for reuse (Op.). Make-up caustic is added to compensate for losses.

The red mud is reworked for recovery of additional amounts of alumina (Pr. and Op.).

In the obtaining of pure Al_2O_3 the *energy requirements* are considerable, since they involve the mining of the crude bauxite and its transportation to the refining plant, which often includes a sea voyage, as from Surinam to Mobile or to East St. Louis. In the refinery, power is needed to operate pumps and calciners; and heat is needed for the calcination of the $Al(OH)_3$ and the concentration of the diluted sodium hydroxide solution from the precipitation. Finally the pure Al_2O_3 must be freighted from the refinery (East St. Louis, Ill., or Mobile, Ala.) to the electrolytic cells at Niagara Falls and elsewhere. However, in the preparation of aluminum the greater energy consumption is in the reaction involved in the reduction of the alumina to aluminum (*cf.* Chap. XVI).

Much study[1] is being directed to the economical production of alumina from clay and other aluminous minerals such as alunite. Separate processes, using alkali or acid leaching, have not been operated long enough to ascertain their competitive positions.

ALUMINUM SULFATE AND ALUMS

The manufacture of alums entails just one step additional to the aluminum sulfate process. This, along with the fact that the uses of aluminum sulfate and alums are similar and the compounds are largely interchangeable, justifies their concurrent discussion. The term *alum* has been very loosely applied. A true alum is a double sulfate of aluminum and a monovalent metal (or radical, such as ammonium). The alums crystallize with 24 molecules of water. Aluminum sulfate is frequently but incorrectly referred to as *water* alum. Chrome alums *have chromium atoms in place of aluminum atoms.*[1]

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[1] ANON., Alumina from Clay, *Chem. Industries*, **54**, 65 (1944); FLEISCHER, Alumina from Alunite, *Chem. & Met. Eng.*, **51**, No. 2, 143 (1944).

Historical.—Alum has been known since ancient times. The writings of the Egyptians mention its use as a mordant for madder and in certain medical preparations. The Romans employed it to fireproof their siege machines and probably prepared it from alunite, $K_2Al_6(OH)_{12}(SO_4)_4$, which is plentiful in Italy.[2]

Uses and Economics.—Alums are used in water treatment and somewhat in dyeing. They have been replaced to a large extent in these applications by aluminum sulfate which has a greater alumina equivalent per unit weight. Pharmaceutically, aluminum sulfate is employed in dilute solution as a mild astringent and antiseptic for the skin. The most important single application of it is in clarifying water, 65 per cent of the total amount manufactured being so consumed. Sodium aluminate, which is basic, is sometimes used with aluminum sulfate, which is acid, to produce the aluminum hydroxide floc.

$$6NaAlO_2 + Al_2(SO_4)_3 + 12H_2O \rightarrow 8Al(OH)_3 + 3Na_2SO_4$$

Second in importance is the application of aluminum sulfate to the sizing of paper. It reacts with sodium resinate to give the insoluble aluminum resinate. For the sizing of paper, aluminum sulfate must be free from ferric iron or the paper will be discolored. The ferrous ions do no harm since they form a soluble, practically colorless resinate which, however, would represent a loss of the resinate. A small amount of aluminum sulfate is consumed by the dye industry as a mordant. Soda alum or aluminum sulfate is used in some baking powders. In 1942, 11,852 short tons of alum and 540,101 short tons of aluminum sulfate were produced in the United States.[3]

Manufacture.—Practically all alums and aluminum sulfate are made now from bauxite by reaction with 60°Bé. sulfuric acid. However, potash alum was first prepared from alunite by the ancients. Other possible sources of alums are shales and other alumina-bearing materials such as clay. Figure 7 illustrates the manufacture of aluminum sulfate. The bauxite is ground until 80 per cent passes 200 mesh, next it is conveyed to storage bins. The reaction occurs in lead-lined steel tanks where the reactants are thoroughly mixed and heated with the aid of agitators and live steam. These reactors are operated in series. Into the last reactor barium sulfide is added in the form of black ash to reduce ferric sulfate to the ferrous state and to precipitate the iron.

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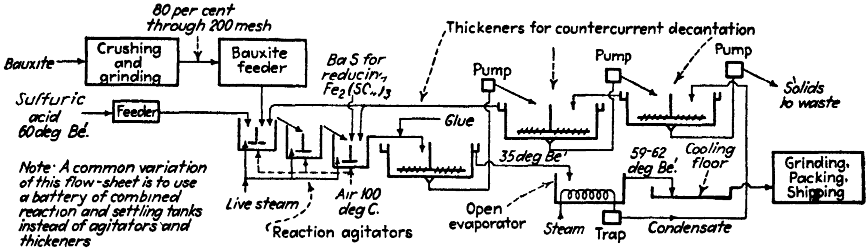
[1] Snell, and Snell, "Chemicals of Commerce," Aluminum Sulfate, p. 103, D. Van Nostrand Company, Inc., New York, 1939.

[2] Partington, "Origins and Developments of Applied Chemistry," p. 148, Longmans, Green and Company, New York, 1935.

[3] Mineral Industry Surveys, *op. cit.*

The mixture from the reactors is sent through a series of thickeners, operated countercurrently, which remove undissolved matter and thoroughly wash the waste so that when discarded it will contain practically no "alum." The clarified aluminum sulfate solution is concentrated in an open, steam-coil-heated evaporator from 35°Bé. to 59 or 62°Bé. The concentrated liquor is poured into flat pans where it is cooled and completely solidified. The solid cake is broken and ground to size for shipping. Another slightly modified procedure uses, instead of reactors and thickeners, combined reaction and settling tanks. The Dalecarlia rapid-sand filter plant which supplies water to Washington, D.C., makes its own filter alum. In this case concentration of liquor would be an unnecessary expense; therefore, the aluminum sulfate is made and used in water solution.[1]


80 per cent through 200 mesh
Bauxite
Crushing and grinding
Bauxite feeder
Sulfuric acid 60 deg Bé.
Feeder
BaS for reducing Fe₂(SO₄)₃
Thickeners for countercurrent decantation
Pump
Pump
Pump
Solids to waste
Glue
35 deg Bé
59-62 deg Bé.
Cooling floor
Grinding, Packing, Shipping
Note: A common variation of this flow-sheet is to use a battery of combined reaction and settling tanks instead of agitators and thickeners
Live steam
Air 100 deg C.
Reaction agitators
Open evaporator
Steam
Trap
Condensate

Bauxite (55 per cent Al_2O_3)	670 lb	Per ton of 17 per cent Al_2O_3 "alum"
H_2SO_4 (60 deg. Bé)	1,140 lb	
Black ash (70 per cent BaS)	13 lb	
Flake glue	0.4 lb.	
Coal (steam)	640 lb.	
Electricity	29 Kw-hr	
Direct labor	1.5 man-hr.	

FIG. 7.—Manufacture of aluminum sulfate by the Dorr procedure.

To make the various true alums, it is necessary only to add the sulfate of the monovalent metal to the dilute aluminum sulfate solution in the proper amount. Concentration of the mixed solution, followed by cooling, yields the alum crystals.

Commercial aluminum sulfate contains only 13 moles of water of crystallization. It is usually in basic form, *i.e.*, there is more alumina present than that theoretically required by the reaction. The chief advantage of basic aluminum sulfate is that it does not rot the burlap bags in which it is shipped as the ordinary product would do.

ALUMINUM CHLORIDE

Aluminum chloride is a white solid when pure. In the presence of moisture, anhydrous aluminum chloride partly decomposes with the evolution of hydrogen chloride. This salt was first prepared in 1825 by H. C. Oersted who passed chlorine over a mixture of alumina and carbon and condensed the vapors of the aluminum chloride formed. Essentially the same process is used today in the commercial preparation of aluminum chloride. The price in 1913 was $1.50 per pound, while the present price is about 5 cents per pound in carload lots.[1]

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[1] LAUTER, Manufacture of Aluminum Sulfate at the Dalecarlia Filter Plant, Washington, D.C., *Ind. Eng. Chem.*, **25**, 953 (1933).

Uses.—Since modern methods of manufacture have reduced the price of aluminum chloride, it has found increasing application in the petroleum industries and various phases of organic technology. It was used to a considerable extent in certain petroleum-cracking processes. Aluminum chloride is a catalyst in alkylation of paraffins and aromatic hydrocarbons by olefins and also in the formation of complex ketones, aldehydes, and carboxylic acid derivatives.

Manufacture.—There are two important methods for the preparation of anhydrous aluminum chloride. One of these is the direct reaction of liquid or gaseous chlorine with metallic aluminum and the second consists of the simultaneous reduction by carbon and chlorination by gaseous chlorine of alumina-bearing materials. The reaction between aluminum and chlorine is exothermic. Enough heat is given off to vaporize the aluminum chloride continuously as it is formed. The reaction between carbon, bauxite, and chlorine, however, is endothermic, and heat must be supplied to cause the reaction to take place. In the United States bauxite is calcined, mixed with a carbonaceous residue, briquetted, and recalcined to drive off all hydrocarbons that would form corrosive hydrogen chloride later on. This material in a shaft kiln is heated up to 1600°C. by a blast of air and chlorinated, the aluminum chloride being volatilized and condensed.

FERROUS SULFATE

Ferrous sulfate is the most abundant of the iron compounds as it is the waste product of the pickling processes in which steel surfaces are cleaned preparatory to electroplating, tinning, galvanizing, or enameling operations. Between 500,000,000 and 800,000,000 gal. of waste liquor, containing on the average 15 per cent ferrous sulfate, are produced annually.[2] This can be evaporated to furnish the ferrous sulfate whenever the market warrants. Unfortunately, no large-scale use has been found for this salt though it has been employed for water clarification by certain cities like St. Louis, Mo. (See Fig. 2, Chap. XIX.)

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[1] McAfee, Cheap Aluminum Chloride, *Chem. & Met. Eng.*, **36**, 422 (1929).

[2] Hodge, Waste Problems of the Iron and Steel Industries, *Ind. Eng. Chem.*, **31**, 1364 (1939); Van Antwerpen, Utilization of Pickle Liquor, *Ind. Eng. Chem.*, **34**, 1138 (1942); Treffler, Manufacture of Ferrous Sulfate, *Chem. Industries*, **54**, 70 (1944), flow chart.

COPPER SALTS

Copper sulfate[1] is the most important compound of copper. Commonly known as *blue vitriol*, it is prepared by the action of sulfuric acid on cupric oxide or sulfide ores. Its poisonous nature is utilized in the insecticide, Bordeaux mixture, which is formed upon the mixing of copper sulfate solution with milk of lime. Copper sulfate is added to water reservoirs occasionally to kill algae. It is employed in electroplating and finds minor applications as a mordant, germicide, and agent in engraving. Certain copper compounds are added to antifouling paints used on ship bottoms.

MOLYBDENUM COMPOUNDS

Molybdenum compounds are not consumed in large tonnage, but they are important in conjunction with hydroxyl compounds like pyrogallol in dyeing furs, feathers, hair, and skins; as lake forming substances with basic dyes; as pigments; and to produce adherence of porcelain enamels to steel. The compounds used for dyes are sodium, potassium, or ammonium molybdates. With basic dyes phospho-molybdic acid is employed. The pigment known as *molybdenum orange* is a mixed crystal of lead chromate and lead molybdate. The compounds used to produce better adherence of enamels are molybdenum trioxide, ammonium, sodium, calcium, barium, and lead molybdates. The mineral raw material is molybdenite, MoS_2, mined at Climax, Colo., which by roasting furnishes a technical grade of molybdenum trioxide, MoO_3, of 80 to 90 per cent purity.

BARIUM SALTS

The most common naturally occurring barium compounds are the mineral carbonate or witherite, which is fairly abundant in England, and the sulfate or barite which is common in certain sections of the United States. The greatest source of barite is Missouri.

Uses.—The applications of barium compounds are varied and important. In 1941, 245,950 short tons of barium chemicals were sold or consumed by producers.[2] *Barium carbonate* is sometimes employed as a neutralizing agent for sulfuric acid and, because both barium carbonate and sulfate are insoluble, no contaminating barium ions are introduced. The foregoing application is found in the synthetic dyestuffs industry. Barium carbonate is a component in some rat poisons and is a minor constituent in crown glass. Witherite is used chiefly to prepare other compounds. *Barium sulfate* is an excellent white pigment particularly in the precipitated form, blanc fixe. It is used as a filler for paper, rubber, linoleum, and oilcloth. Because of its opacity to X rays, barium sulfate, in a purified form, is important in contour photographs of the digestive tract. The paint industry is the largest single consumer of barium compounds. Barium sulfide and zinc sulfate solutions are mixed to give a precipitate of barium sulfate and zinc sulfide, which is given a heat-treatment to yield the cheap but good pigment, *lithopone*, as described in Chap. XXIV. Barium chlorate and nitrate are used in pyrotechnics to impart a green flame. Barium chloride is applied where a soluble barium compound is needed. Barium saccharate is used by a large beet-sugar group for sugar recovery from discard molasses (Chap. XXX).

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[1] SNELL and SNELL, *op. cit.*, pp. 124–127; PERRY, *op. cit.*, p. 1936.

[2] Mineral Industry Surveys, *U.S. Bur. Mines*, M.M.S. 1016, August, 1942.

Manufacture.—The preparation of soluble barium salts is simple where witherite is available. The only steps necessary are treatment with the proper acid, filtration to remove insoluble impurities, and crystallization of the salt. Since there is little witherite in the United States, barium salts are prepared from barite. The high-temperature reduction of barium sulfate with coke yields the water-soluble barium sulfide which is subsequently leached out. The treatment of barium sulfide with the proper chemical yields the desired barium salt. Purification of the product is complicated by the impurities introduced in the coke. Pure barium carbonate and barium sulfate are made by precipitation from solutions of water-soluble barium salts. Much barite is ground,[1] acid-washed, lixiviated, and dried to produce a cheap pigment or paper or rubber filler.

STRONTIUM SALTS

There are only two important, naturally occurring ores of strontium: strontianite (strontium carbonate) and celestite (strontium sulfate). Large deposits of both were formerly found in Germany, but the strontianite, being the more readily utilizable, has been practically exhausted. The United States and England have considerable deposits of celestite.

Uses.—Few of the strontium compounds are of commercial importance. Strontium hydroxide is a moderately strong base which forms an insoluble compound with sucrose. This reaction makes possible the recovery of sucrose from beet molasses containing much uncrystallizable invert sugar. This process is employed in Europe. Strontium nitrate is used in pyrotechnics to impart a brilliant carmine-colored flame. Strontium carbonate is an ingredient of special glass and serves for the manufacture of other strontium compounds.

Manufacture.[2]—In localities where strontianite is available, strontium salts are prepared by treatment of the mineral with the proper acid.

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[1] PERRY *op. cit.*, p. 1952, for grinding; p. 1692 for filtration.

[2] SNELL and SNELL, *op. cit.*, pp. 84–85.

Where celestite is obtainable and strontianite is not, the finely ground celestite is converted to the carbonate by boiling with 10 per cent sodium carbonate solution.

$$SrSO_4 + Na_2CO_3 \rightarrow SrCO_3 + Na_2SO_4$$

Practically a quantitative yield of strontium carbonate (insoluble) and sodium sulfate (soluble) results. The celestite may need to be purified before treatment with the sodium carbonate, however, if a pure carbonate is desired. By reaction of the strontium carbonate with appropriate acids, the various salts result.

BORON COMPOUNDS

The important, naturally occurring ores of boron have been colemanite, $Ca_2B_6O_{11}\cdot 5H_2O$; tincal, $Na_2B_4O_7\cdot 10H_2O$; and boracite, $2Mg_3B_8O_{15}\cdot MgCl_2$. However, boron-containing brines and kernite, $Na_2B_4O_7\cdot 4H_2O$, are the present sources in the United States.

Uses.—The most important compound for industrial use is borax, $Na_2B_4O_7\cdot 10H_2O$. It is widely used as a flux, in the manufacture of Pyrex glass, in the making of glazes and enamels, in the preparation of soaps, and other miscellaneous processes. Boric acid, H_3BO_3, is a weak acid that is applied medicinally as a mild antiseptic and also finds some consumption in the manufacture of glazes and enamels for pottery. Boron carbide, B_6C, is the hardest artificial abrasive known.

Manufacture.—Most of the borax in the United States is prepared either from the mineral kernite found in the Mohave Desert of California or from the saline brines of Searles Lake. As mined, kernite contains considerable clay which is removed by dissolving in water, filtering, and crystallizing. Borax is recovered along with potassium chloride from the brines of Searles Lake.[1]

SILVER NITRATE

Silver nitrate (lunar caustic) is used in surgery, as a laboratory reagent, in hair dyes, and in laundry marking inks. When it is allowed to come in contact with skin, hair, or cloth, it is reduced to metallic silver, thus leaving a gray to black stain. The largest consumption is, however, in the photographic industry where silver nitrate is the source of the various sensitive silver halides of the emulsion. It is prepared by dissolving metallic silver in dilute nitric acid in porcelain vessels, evaporating, and crystallizing.

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[1] Description and flow chart are in Chap. XIII for the plant of the American Potash and Chemical Company; also on Searles Lake is the borax plant of the West End Chemical Company.

RADIUM AND URANIUM SALTS

The discovery of radium and its isolation by the Curies was one of the greatest events of all time. Marie Curie noticed that certain samples of uranium ore exhibited greater radioactivity than was to be expected from the uranium content. After a long series of concentrating operations based upon partial crystallization, the Curies discovered and isolated polonium first and then, in 1898, radium.

Uses.—The most important single application of radium has been medical. Its valuable curative properties on cancerous growths and in certain other morbid conditions are well known even to the layman. To a certain extent X rays have been substituted for radium. The only other common use for radium is in the manufacture of luminous paints for watch or clock numerals and hands wherein minute quantities of a radium salt are mixed with zinc or calcium sulfide. However, the discovery of radium and its properties has completely transformed the fundamental concepts of chemical elements and, hence, has affected the philosophical view of the universe.

Manufacture.—Radium occurs with uranium, of which it is a disintegration product. The Curies isolated radium from the mineral, pitchblende, where it is found in the proportion of 1 part of radium to each 3,000,000 parts of uranium occurring as uraninite, U_3O_8. Pure uraninite, therefore, would yield 1 g. of radium for each 3.88 tons.

For a time radium was produced in the United States from carnotite, a sandstone cemented together by uranium vanadate. Since the early twenties these ores have not been worked. Even after hand sorting, the choice carnotite ore averaged only 2 per cent equivalent U_3O_8 and could not compete with the rich ores from the Belgian Congo. The methods employed for the extraction of radium from carnotite are described in the literature.[1]

For many years the Belgians had a world monopoly on radium production, until the discovery of the rich pitchblende deposits on the eastern shore of the Great Bear Lake, Northwest Territories, Canada. The refining methods successful for the Canadian ores are adaptations of those introduced by the Curies. The ore is hand-picked at the mines. Seven tons of chemicals are needed to treat 1 ton of ore. For this reason, the ore is shipped to the nearest point at which these chemicals are readily available, Port Hope, Ontario. After fine grinding, the ore is subjected to a differential settling operation in which the valuable concentrate settles to the bottom.

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[1] VIOL, The Commercial Production and Uses of Radium, *J. Chem. Education*, **3**, 757 (1926).

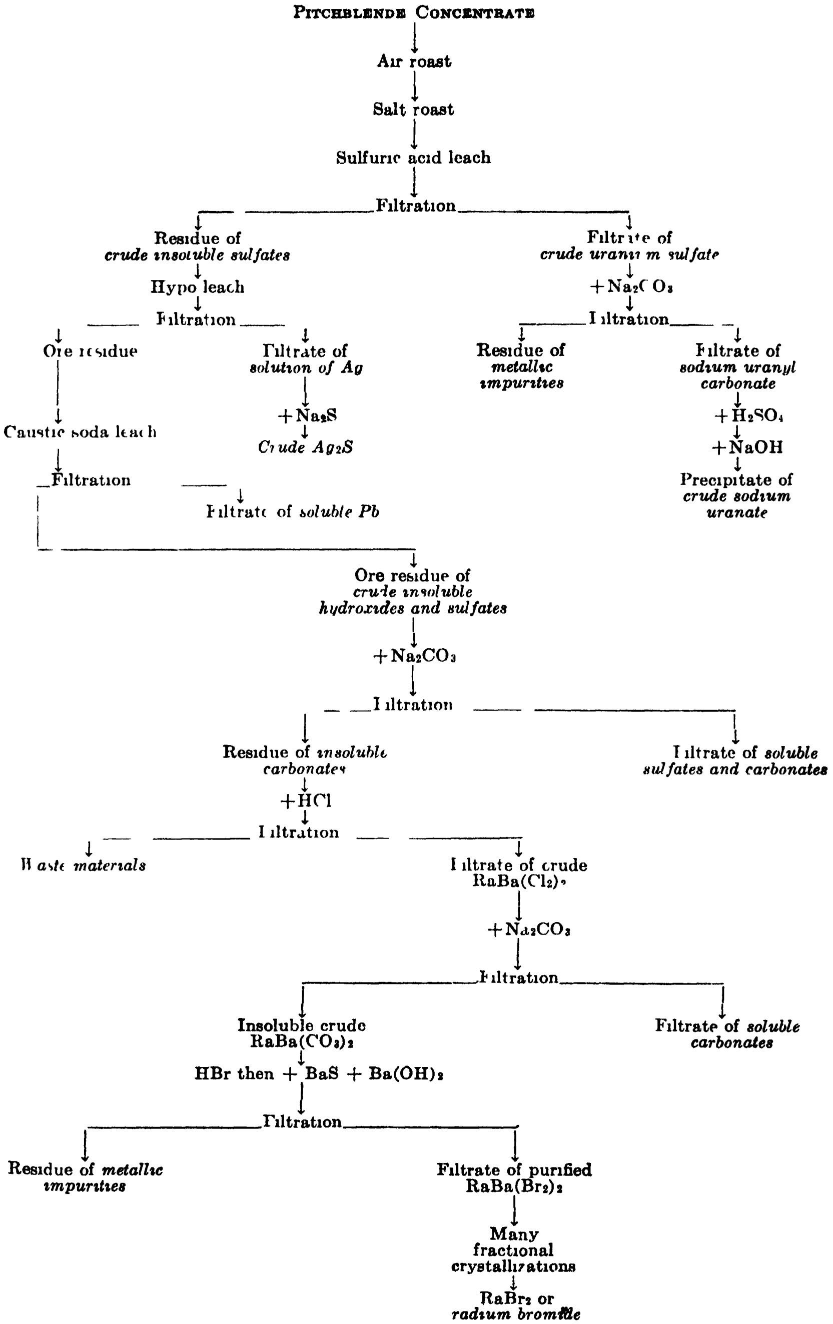
Pitchblende Concentrate
Air roast
Salt roast
Sulfuric acid leach
Filtration
Residue of crude insoluble sulfates
Hypo leach
Filtration
Ore residue
Caustic soda leach
Filtration
Filtrate of soluble Pb
Filtrate of solution of Ag
+Na₂S
Crude Ag₂S
Filtrate of crude uranium sulfate
+Na₂CO₃
Filtration
Residue of metallic impurities
Filtrate of sodium uranyl carbonate
+H₂SO₄
+NaOH
Precipitate of crude sodium uranate
Ore residue of crude insoluble hydroxides and sulfates
+Na₂CO₃
Filtration
Residue of insoluble carbonates
+HCl
Filtration
Waste materials
Filtrate of crude RaBa(Cl₂)₂
+Na₂CO₃
Filtration
Insoluble crude RaBa(CO₃)₂
HBr then + BaS + Ba(OH)₂
Filtration
Residue of metallic impurities
Filtrate of purified RaBa(Br₂)₂
Many fractional crystallizations
RaBr₂ or radium bromide
Filtrate of soluble carbonates
Filtrate of soluble sulfates and carbonates

Fig 8 —Radium and uranium separation from pitchblende.

Figure 8 outlines the various steps necessary to produce pure radium-barium bromide from the ore concentrate. The air roast decomposes *sulfides and carbonates that would froth if treated directly with sulfuric* acid. The salt roast stabilizes the silver as insoluble silver chloride. The sulfuric acid leach dissolves out the uranium and some of the metallic impurities. The residue left after the filtration consists chiefly of insoluble sulfates which are then treated with thiosulfate to dissolve the silver chloride. After another filtration the residue is given a caustic soda leach which changes the lead sulfate to the soluble sodium plumbate. Subsequent treatment of the mixture of hydroxides and sulfates with sodium carbonate releases certain soluble sulfates and carbonates which are filtered off. The residue now consists wholly of carbonates and some impurities. The latter are insoluble in hydrochloric acid. The filtrate containing crude radium-barium chloride is treated with sodium carbonate which precipitates the radium and barium ions but leaves soluble impurities in solution. The carbonates are converted to bromides by hydrobromic acid. Barium sulfide and barium hydroxide are used to precipitate traces of impurities. The remaining work consists of tedious fractional crystallizations by each of which the radium concentration is raised slightly until the final product contains 90 to 95 per cent radium bromide.[1]

Radium bromide is sold in 10-mg. lots sealed in glass tubes which are then placed in lead cylinders. The price in 1940 of a single vial was $3,000.

RARE-EARTH COMPOUNDS

The rare earths comprise a series of 15 elements so nearly identical in properties that they are separated only with difficulty. Cerium and thorium are the most important commercially. Although rare earths occur in certain minerals native to the Carolinas, these minerals have not been able to compete with the richer monazite sands found in Brazil. Preliminary separation is accomplished by the use of jigging, where the valuable material is denser than the worthless fraction. The concentrates are leached with hot sulfuric acid of strength greater than 66°Bé. The rare-earth metal compounds are precipitated by dilution of the sulfuric acid solution. The usual practice is to isolate thorium and cerium hydroxides, the latter containing all the other rare earths except thorium unless careful and tedious purifications are carried out.

Crude cerium hydroxide is employed in flaming arc carbons, and the purified form imparts a yellow color to glass. A large use for thorium and cerium is in gas mantles. Metallic cerium alloyed with iron gives pyrophoric alloys.[1] Gas mantles are prepared by the impregnation of cotton, ramie fiber, or silk fabrics with a mixture comprising 99 per cent thorium nitrate and 1 per cent cerium nitrate in aqueous solution. After impregnation and drying, the mantle is ignited to burn away all organic matter and to convert the nitrates to the oxides. The finished mantle is very fragile and is coated with collodion which burns away at once when the mantle is first put into use.[2]

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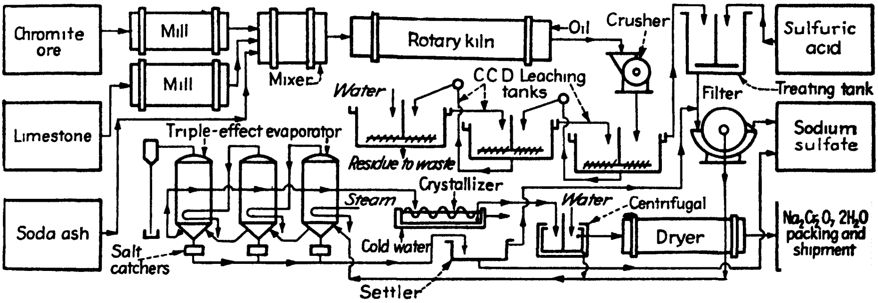
[1] KUEBEL, Extraction of Radium from Canadian Pitchblende, *J. Chem. Education*, **17, 417 (1940).**

SODIUM DICHROMATE

The starting material for the manufacture of sodium dichromate and other chromium compounds is chromite, a chromium iron oxide containing approximately 50 per cent Cr_2O_3, the balance being principally FeO, Al_2O_3, SiO_2, and MgO. There are no high-grade chromite deposits in the United States, and most of the ore used in the chemical industry is imported from South Africa. In war years it has been proposed that domestic ore[3] should be used. Much sodium dichromate is consumed as the starting material for making, by glucose reduction, the solutions of chromium salts employed in chrome leather tanning (Chap. XXV) and in chrome mordant dyeing of wool cloth. Certain pigments, as the yellow lead chromate, are manufactured basically from sodium dichromate as are also the green chromium oxides for ceramic pigments. Much chromium enters the metal field as stainless steel and other high-chromium alloys and for chromium plating of other metals.



Chromite ore	1.1 ton	Fuel oil	130 gal		
Limestone	1.5 ton	Steam	6,000 lb		
Soda ash	0.8 ton	Electricity	500 kw-hr		
Sulfuric acid, 66°Bé	0.45 ton	Direct labor	15 man-hr		

} To produce 1 ton sodium dichromate and 0.6 ton sodium sulfate anhydrous

FIG. 9.—Flow chart for sodium dichromate from chromite ore.

The ore is ground to 200 mesh, mixed with ground limestone and soda ash, and roasted at approximately 2200°F. in a strongly oxidizing atmosphere. The sintered mass is crushed and leached with hot water to separate the soluble sodium chromate. The solution is treated with enough sulfuric acid to convert the chromate to dichromate with the resulting formation of sodium sulfate. Most of the sodium sulfate crystallizes in the anhydrous state from the boiling-hot solution during acidification, and the remainder drops out in the evaporators on concentrating the dichromate solution. From the evaporator the hot saturated dichromate solution is fed to the crystallizer, then to the centrifuge and drier (see Fig. 9).

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[1] SNELL and SNELL, *op. cit.*, p. 149.

[2] ANON., Industrial Excursions, A. C. S. Philadelphia meeting, 1919; The Welsbach Company Plant, *Chem. & Met. Eng.*, **21**, 497 (1919).

[3] ANON., Producing Chromate Salts from Domestic Ores, *Chem. & Met. Eng.*, **47**, 688 (1940), flow chart.

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CHAPTER XXII

EXPLOSIVES, PYROTECHNICS, AND CHEMICAL WARFARE

INDUSTRIAL AND MILITARY EXPLOSIVES

Many professional chemists and chemical engineers tend to view the subject of explosives from a purely military standpoint. It should always be remembered that, although explosives have contributed much to the destruction of man, they have also enabled him to perform many great engineering feats which would have been physically or economically impossible without their use. The building of such large engineering projects as Boulder Dam and the Holland Tunnel would have taken hundreds of years if performed by hand labor alone. Explosives are among the most powerful slaves that man has learned to employ. Mining of all kinds depends on blasting, as does such a prosaic but necessary act as the clearing of stumps and large boulders from land. Even the digging of holes for tree planting and ditches for drainage is quickly, efficiently, and cheaply done by means of dynamite—and with less effort than by any other method. Approximately 85,000,000 acres of muck and swampland have been drained by propagated ditch blasting using dynamite.[1] Already rivets are being installed in airplane construction by means of an explosive[2] in the shank, which is fired by heat, with the consequent saving of much time and effort.

Uses and Economics.—In peacetime large quantities of explosives are consumed for normal technical operations as listed in Table 1; in times of war tremendous quantities are required. During the First World War it required an average of 2 to 5 tons of munitions to accomplish a single casualty.

Classification.—An explosive is a material which, under the influence of thermal or mechanical shock, decomposes rapidly and spontaneously with the evolution of a great deal of heat and much gas. The hot gases cause extremely high pressure if the explosive is set off in a confined space. Explosives differ widely in their sensitivity and power. Only those of a comparatively insensitive nature, capable of being controlled and having a high energy content, are of importance commercially or in a military sense.

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[1] *Du Pont Magazine*, October, 1941.

[2] *Du Pont Magazine*, p. 8, Midsummer, 1941.

For purposes of classification it is convenient to place explosives in three distinct divisions:

1. Initiating or primary explosives (detonators)—lead azide, mercury fulminate, diazodinitro-phenol, lead styphnate (lead trinitro-resorcinate).
2. High explosives—trinitro-toluene (T.N.T.), amatols, pentaerythritol-tetranitrate, cyclonite (hexogen or R.D.X.), tetryl, dynamites, nitro-starch.
3. Low explosives or propellants—colloided cellulose nitrate (smokeless powder), black powders.

TABLE 1.—CLASSES OF EXPLOSIVES USED IN DIFFERENT INDUSTRIES,[a] 1941
(In pounds)

Purpose for which used	Black blasting powder	High explosives, other than permissibles	Permissible explosives	Total
Coal mining:				
Bituminous	49,028,225	20,770,300	55,570,072	125,368,597
Anthracite	4,474,275	17,745,090	14,401,061	36,620,426
Total	53,502,500	38,515,390	69,971,133	161,989,023
Metal mining	58.525	116,343,629	19,125	116,421,279
Quarrying	3,100,150	78,403,268	550,925	82,054,343
Railway and other construction	2,593,450	108,526,853	32,587	111,152,890
All other purposes	202,950	10,068,313	38,439	10,309,702
Total	59,457,575	351,857,453	70,612,209	481,927,237

[a] ADAMS and WRENN, Production of Industrial Explosives in the United States, *U.S. Bur. Mines, Tech. Paper* 647, 1942. The above figures represent a large increase over 1940 when the total was 423,369,230 lb.

Initiating or *primary explosives* are quite sensitive materials which can be made to explode by the application of fire or by means of a slight blow. They are very dangerous to handle and are used in comparatively small quantities to start the explosion of larger quantities of less sensitive explosives. Initiating explosives are generally used in primers, detonators, and percussion caps.

High explosives are materials which are quite insensitive to both mechanical shock and flame but which explode with great violence when set off by an explosive shock such as that which would be obtained by detonating a small amount of an initiating explosive in contact with the high explosive. In the case of high and primary explosives, decomposition proceeds by means of a detonation, which is a rapid chemical destruction progressing directly through the mass of the explosive. This detonation is thought to be a chain reaction and proceeds at rates that are frequently as high as 20,000 ft. per sec. for high-velocity dynamites. It is this high rate of energy release rather than the total energy given off that makes a product an explosive. Nitro-glycerine has only one-eighth the potential energy of gasoline. On the other hand, most high explosives, when unconfined or unshocked, will merely burn if ignited.

Low explosives, or *propellants,* differ in their mode of decomposition from the two other types; they only burn. Burning is a phenomenon that proceeds not through the body of the material but in layers parallel to the surface. It is quite slow in its action, comparatively speaking, rarely exceeding 0.25 m. per sec. The action of low explosives is, therefore, less shattering. Low explosives evolve large volumes of gas on combustion in a definite and controllable manner.

The industrial classification used in Table 1 is that of the U.S. Bureau of Mines where *black blasting powder* refers to all black powder having sodium or potassium nitrate as a constituent. Here *permissible explosives* include ammonium nitrate explosives, hydrated explosives, organic nitrate explosives, and certain nitro-glycerine explosives that contain an excess of free water or carbon. The permissible explosives must pass certain tests[1] to ensure a minimum of flame and temperature to reduce fires in coal mines where 99 per cent of the permissibles are employed. Ammonium nitrate constitutes over 65 per cent of the weight of the permissibles. The *high explosives* used in industries are the usual dynamites.

Properties of Explosives.—In order to compare explosives, certain standard tests have been worked out to measure their properties. These tests are empirical and are of value only for purposes of comparison. The results of some of these tests are shown in Table 2 and include also military explosives.

The *power* or *brisance* of an explosive may be measured by exploding a small quantity of it in a *sand bomb,* which is a heavy-walled vessel designed to resist the explosion without being ruptured. It contains 200 grams of Ottawa silica sand,[2] all of which passes through a 20-mesh sieve and all of which is retained on a 30-mesh sieve. The explosive is immersed in the sand and the bomb closed. After the explosion, the sand is sieved and the weight of sand passing through the 30-mesh screen is taken as a measure of the power of the explosive being tested. Another test of a somewhat similar nature is the *Trauzl block test.* This test measures the power of the explosive by measuring the ballooning of a soft lead cylinder in which the explosive is inserted and exploded. The standard Trauzl block is 200 mm. in diameter and 200 mm. high with a central hole 25 mm. in diameter and 125 mm. deep. Ten grams of the explosive is used in making the test and the results are reported in terms of the cubic centimeters of increase in volume caused by detonation of the explosive. Both of these tests furnish an indication of the *brisance* (from French *briser*, to shatter) or shattering power of the high explosive being tested. This *brisance*, or shattering effect, is probably a combination of the strength and the velocity.

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[1] U.S. Bureau of Mines, Explosives Division, Active List of Permissible Explosives and Blasting Devices, *U.S. Bur. Mines, Rept. Investigations* 3471, 1939.

[2] This sand is selected for its uniformity. It is mined at Ottawa, Ill. For details of testing explosives, see references at end of this chapter, particularly the book by Meyer for an over-all presentation.

The *sensitivity* of an explosive to *impact* is determined by finding the height from which a standard weight must be allowed to fall in order to detonate the explosive. This test is of greatest importance in the case of initiating explosives.

Table 2.—Summary of Characteristics of Explosives[a]

Name	Formula	Products per formula weight	Qv, Cal. per kg.	Te, °C.	f, kg. per sq. cm.	V, m. per sec.	Trauzl expansion, cc. per 10g.	Potential × 10^6 kg. per m.
Gunpowder.......	$2KNO_3 + 3C + S$	$N_2 + 3CO_2 + K_2S$	501	2090	2,970	.....	30	2.1
Nitro-cellulose.....	$C_{24}H_{29}O_9(NO_3)_{11}$	$20.5CO + 3.5CO_2$ $+ 14.5H_2O$ $+ 5.5N_2$	1,250	2800	10,000	6,100	420	5.3
Nitro-glycerine....	$C_3H_5(NO_3)_3$	$3CO_2 + 2.5H_2O$ $+ 1.5N_2$ $+ 0.25O_2$	1,526	3360	9,835	8,500	590	6.5
Ammonium nitrate	NH_4NO_3	$2H_2O + N_2$ $+ 0.5O_2$	384	1100	5,100	4,100	300	1.6
T.N.T............	$C_7H_5(NO_2)_3$	$6CO + C + 2.5H_2$ $+ 1.5N_2$	656	2200	8,386	6,800	260	2.8
Picric acid........	$C_6H_2(OH)(NO_2)_3$	$6CO + H_2O$ $0.5H_2 + 1.5N_2$	847	2717	9,960	7,000	300	3.6
Ammonium picrate	$C_6H_2(NO_2)_3ONH_4$	$6CO + H_2O$ $+ 2H_2 + 2N_2$	622	1979	8,537	6,500	230	2.6
Tetryl..	$C_7H_5N_5O_8$	$7CO + H_2O$ $+ 1.5H_2$ $+ 2.5N_2$	908	2781	10,830	7,229	320	3.9
Mercury fulminate	$Hg(ONC)_2$	$Hg + 2CO + N_2$	420	4105	5,212	3,920	213	1.8
Lead azide........	PbN_6	$Pb + 3N_2$	684	3180	8,070	5,000	250	2.9

[a] By permission, from p. 439 of Meyer, "The Science of Explosives," The Thomas Y. Crowell Company, New York, 1943.

The heat of explosion is given in Table 2 as *Qv*. This is the heat evolved at constant volume. In comparison with heats of combustion of ordinary fuels, this is comparatively small in the number of calories. An explosive, however, exerts all this energy extremely rapidly. In the same table, *Te* is the *explosion temperature*. The *specific pressure*, designated in the table as *f*, signifies the pressure exerted by 1 kg. of explosive in volume of 1 l. at the explosion temperature of *Te*. *Potential* equals 425*Qv* kg.-m. where 425 is the mechanical equivalent of heat. This measures the total capacity for work in units of mechanical energy.

The *velocity* (V in the table) of the *detonation wave* in a column of explosive may be determined by threading wires across the column. These wires are connected through an electrical circuit in such a manner that, when they are broken by the moving wave, they cause a spark to jump onto the surface of a sooted drum revolving at a high, constant speed. The distance between the marks made by the sparks on the rotating drum, the distance between the wires inserted in the column of explosive, the diameter and speed of rotation of the drum all being known, it is a simple matter to calculate the velocity of detonation. Recently, methods have been developed for determining the velocity of detonation by means of high-speed photography. The velocity of detonation is dependent on many factors including the composition of the explosive, the density at which it was loaded before firing, and the degree of confinement. It is, however, constant for a given explosive under fixed conditions.

Certain accelerated aging tests are frequently run to determine the *stability* of explosives on storage. The time required for the evolution of traces of oxides of nitrogen at a comparatively high temperature is most frequently used for this purpose. Such tests are difficult to correlate with storage life.

It is important that explosives for use in mines, particularly coal mines, be of such a type that they evolve no poisonous gases on explosion and produce a minimum of flame. This latter requirement is necessary in order that the explosive be incapable of igniting mixtures of air and coal dust, or air and methane (firedamp), which inevitably occur in coal mines. Explosives for mine use are tested and their properties specified by the U.S. Bureau of Mines and are commonly known as *permissibles*. Permissibles differ from other explosives, particularly black powder, most markedly in the fact that they produce a flame of small size and extremely short duration. Permissibles contain coolants to regulate the temperatures of their flames and hence further reduce the possibility of their ignition of combustible mixtures. Permissibles are tested by explosion in a long gallery filled with coal dust, air, and methane. They should not explode this mixture.

MILITARY EXPLOSIVES

As the requirements for military explosives are extremely strict, only a few of them have survived the competitive testing. In this connection it is fundamental to understand the construction of a high-explosive artillery shell as depicted in Fig. 1. Such a shell consists of a thin brass or steel cartridge case holding the primer, igniter, and propellant charge. This case is designed to fit smoothly into the gun and, on explosion, to expand (obdurate), sealing the breech of the gun so that the escape of gases from the burning of the propellant charge is prevented and thus allowing the full effect of the propellant to be exerted on the projectile or destructive half of the shell.

The *primer* contains a small amount of a primary explosive or sensitive mixture (*e.g.*, mercury fulminate or a mixture such as $KClO_3$ + $Pb(CNS)_2$ + Sb_2S_3 + T.N.T. + ground glass). This mixture explodes under the impact of the firing pin and produces a flame which ignites the black powder[1] charge in the *igniter*, which in turn ignites the *propellant* charge of smokeless powder. The burning of the smokeless powder causes the rapid emission of heated gas which ejects the *projectile* from the gun. On impact with the target, the mechanism of the *fuze* sets off a small quantity of a primary explosive (*detonator*) which causes the explosion of the *booster*—an explosive of intermediate sensitivity (between that of a primary explosive and the bursting charge, *e.g.*, tetryl), which picks up the explosive wave from the primary explosive, amplifies it, and ensures the complete detonation of the bursting charge. The *bursting charge* or high explosive is usually T.N.T. or 50/50 amatol, 50 per cent NH_4NO_3 + 50 per cent T.N.T., for ordinary use and ammonium picrate for armor-piercing shell.

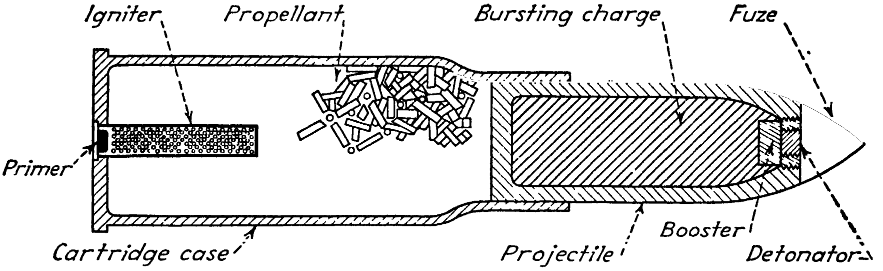

FIG. 1.—Complete round of high explosive ammunition.

Projectiles designed for *armor piercing* must have heavy walls and contain an explosive so insensitive to impact that it can withstand the passage of the shell through the armor plate and not explode until the shell has penetrated it. Ammonium and guanidine picrates are the two explosives most suitable for this purpose. Special projectiles loaded with lead balls embedded in a matrix of rosin or bakelite and equipped with a time fuze causing them to explode in mid-air are known as *shrapnel.*[2] Some projectiles contain war gas in place of the bursting charge. In this case the booster acts to break open the shell case and scatter the chemical casualty-producing agent.

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[1] Black powder is easy and smokeless powder difficult to ignite; therefore, black powder is frequently used to ignite smokeless powder.

[2] The original shrapnel is considered obsolete. Popular opinion now applies the name *shrapnel* to any type of high-explosive shell fragmenting in mid-air, *e.g.*, antiaircraft shell.

Nitro-cellulose.[1]—The explosive properties of nitrated cotton were recognized at an early date and attempts were made to adapt this material as a military propellant. These early attempts were abortive, for, because of the large amount of surface of the nitrated cotton, the combustion was far too rapid and uncontrollable for propellant use. Many lives were lost during these early experiments. The discovery of methods of colloiding the material into a dense uniform mass of resinous appearance removed this difficulty and, with the discovery of suitable stabilization methods to prolong its storage life, nitro-cellulose soon pushed black powder out of use as a military propellant.

The cellulose molecule is a highly complicated[2] one with a molecular weight that is frequently as high as 300,000. Any given sample of cellulose will contain a wide distribution of molecular weights all having the empirical formula $[C_6H_7O_2(OH)_3]_n$. There are thus three hydroxyl groups per fundamental (glucose) unit that may be esterified with nitric acid, indicating a possible nitrogen content of 14.16 per cent which is higher than any commercially used product. The reaction may be formulated:

$$C_6H_7O_2(OH)_3 + 3HONO_2 + H_2SO_4 \rightarrow C_6H_7O_2(ONO_2)_3 + 3H_2O + H_2SO_4$$

Celluloses that have not been nitrated completely to the trinitrate are used for the various industrial cellulose nitrates as shown in Fig. 2. In addition to the nitrate esters, some sulfate esters are formed by the sulfuric acid which is added to tie up the water resulting from the nitration reaction and to permit the reaction to progress to the right. These sulfate esters are unstable, and their decomposition would give rise to a dangerous acid condition in the stored powder if not removed. These sulfate esters are decomposed in the poaching process.

The finished nitro-cellulose should not be allowed to become acid in use or storage as this catalyzes its further decomposition. A stabilizer is, therefore, added which reacts with any trace of nitrous, nitric, or sulfuric acid that may be released due to the decomposition of the nitro-cellulose and thus stop further decomposition. For smokeless powder diphenylamine is used (diphenylurea in Great Britain) and for celluloid, urea.

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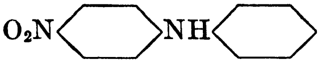
[1] Although the word *nitro-cellulose* is commonly used for nitrated cellulose fiber, it should be noted that the material is not a nitro compound but a true nitrate ester. The name *cellulose nitrate* is therefore chemically more proper, but nitro-cellulose is much more widely employed in technical spheres.

[2] *Cf.* WHITMORE, "Organic Chemistry," p. 587, D. Van Nostrand Company, Inc., New York, 1937; KRAEMER, *Ind. Eng. Chem.*, **30**, 1200 (1938).

The diphenylamine forms a series of innocuous compounds with the evolved gases of which the following are examples:



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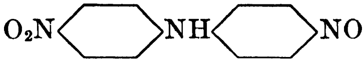

The commercial manufacture of cellulose nitrate is illustrated in Fig. 3 where the following *unit operations* (Op.) and *unit processes* (Pr.) are involved:

Cotton linters or specially prepared wood pulp[1] is purified by boiling with dilute caustic solution (Pr.). See Fig. 2 for purification details.

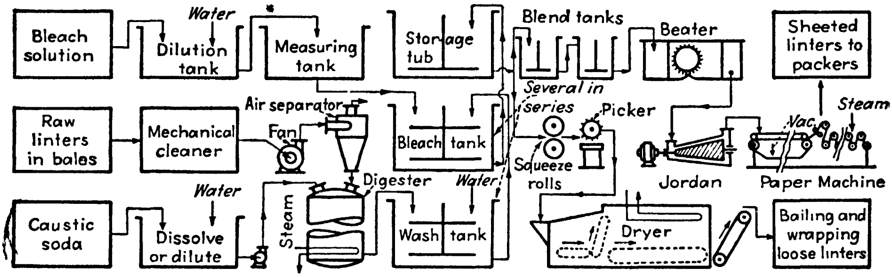

FIG. 2.—Flow sheet for chemical cotton.

Bleaching is effected with CaCl·OCl or NaOCl (Pr.).

The cotton is dried, fluffed, and weighed (Op.).

Mixed acid is made up from fortifying acid and spent acid, brought to proper temperature and run into the nitrator (Op.).

Nitration (esterification) is usually conducted under carefully controlled conditions in a "mechanical dipper" nitrator (Pr.).

32 lb. of purified and dried cotton linters form one nitrator charge. The cotton is agitated with approximately 1,500 lb. of mixed acid at 30°C. for about 25 min. The composition of the acid used averages: HNO_3, 21 per cent; H_2SO_4, 63 per cent; N_2O_4, 0.5 per cent; H_2O, 15.5 per cent.

The entire nitrator charge is dropped into a centrifugal where the spent acid is centrifuged from the nitrated cellulose (Op.).

The spent acid is partly fortified for reuse and partly sold or otherwise disposed of as by denitration and concentration of the sulfuric acid (Op. and Pr.).

The nitrated cotton is drowned with water, washed by boiling and in a beater (Op.).

In order to produce a smokeless powder more stable on storage, the following purification is employed in these two steps and the poaching, to destroy unstable sulfate esters and completely to remove free acid: (1) 40 hr. of boiling with at least four changes of water, (2) pulping of fiber by means of a beater or a Jordan engine followed by

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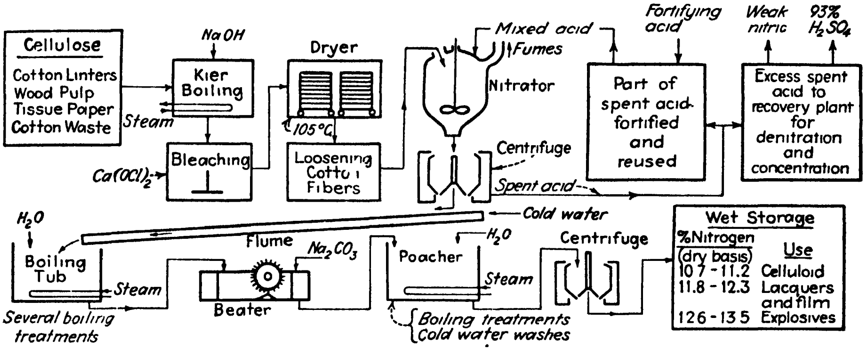
[1] Cotton linters are considered to be the purest form of cellulose fiber available and hence are most desirable for a starting material. Other cellulose material is nitrated, including waste cotton and specially purified sulfite pulp or paper. A pictured flow sheet for linters production is given by *Chem. & Met. Eng.*, **48,** No. 4, 108 (1941), and a pictured flow sheet for smokeless powder by *Chem. & Met. Eng.*, **49,** No. 4, 76 (1942).

Poaching of the washed nitrated cotton by boiling first with a dilute Na_2CO_3 solution (5 lb. soda ash per ton of the cellulose nitrate) and then with many washes of boiling pure water (Pr.).

The poached nitro-cellulose is freed of most of its water by centrifugation. This usually results in a water content of approximately 28 per cent (Op.).



Cotton Linters	0 75 lb	Per pound dry cellulose nitrate (0 75 lb raw cotton furnish about 0 6 lb of purified cotton fibers)
HNO_3 (100%)	1 0 lb	
H_2SO_4 (100%)	0 5 lb	
Na_2CO_3	0 002 lb	
Chlorine	Variable but small	
Water	5 0 gal	
Direct Labor	0 03 man-hr	

Note:
Nitrogen content of cellulose nitrate controlled by composition of nitration mixed acid
Quality of product depends on grade of cellulose used and care devoted to manufacturing procedures
Steps shown used for military product In use wet product is dried by alcohol displacement

FIG. 3.—Flow sheet for nitro-cellulose (cellulose nitrate).

At this point the nitro-cellulose is usually stored until desired and the complete laboratory examination can be made (Op.).

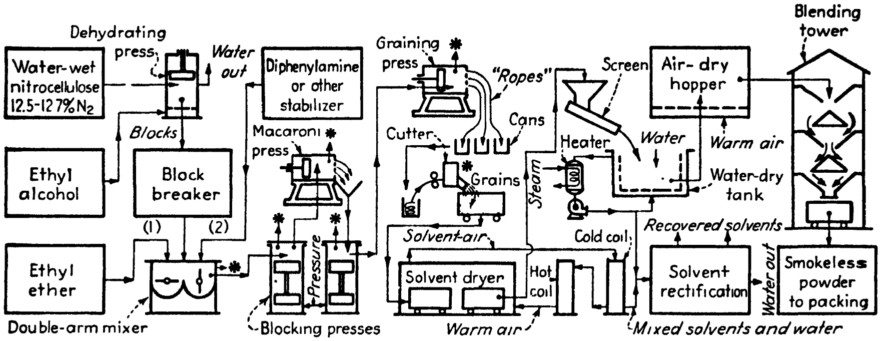
The water content of the nitrated cotton is reduced to a low figure by alcohol percolation under pressure dehydration (Op.).

The nitrated cellulose is disintegrated, then "colloidized" by mixing with alcohol, ether, diphenylamine, and other modifying agents (Op.).

Grains are formed by extrusion through dies and these are dried and blended to form smokeless powder (Op.), see Fig. 4.

The nitro-cellulose produced in this manner contains about 12.6 per cent nitrogen and is known as *pyrocotton.* By using a stronger acid, the nitrogen content may be made as high as 13.6 per cent nitrogen. Cotton nitrated to contain 13.2 per cent nitrogen or greater is known as *guncotton.* Modern military smokeless powder contains about 13.15 per cent nitrogen and is made from a blend of pyro- and guncotton.

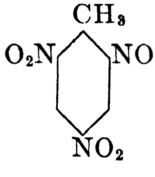
Smokeless powder is colloided nitro-cellulose containing about 1 per cent of diphenylamine to improve its storage life and a small amount of a plasticizer (*e.g.*, dibutyl phthalate). The manufacturing sequences are given by Fig. 4. Modifying agents such as dinitro-toluene and certain inorganic salts are sometimes added in order to reduce the flash of the gun in which the powder is used and to minimize the hygroscopicity of the powder. In the United States the colloiding is usually accomplished by pumping ethyl alcohol through the wet nitro-cellulose in a hydraulic press to remove the water (this makes a drying process unnecessary), adding ether, and macerating in a dough mixer. This combination of alcohol and ether reduces the nitro-cellulose to a pulpy mass which may be extruded into rope and cut to a definite length to give powder grains. It should be noted that neither alcohol nor ether alone will colloidize the nitro-cellulose, but the combination (1 part alcohol to 2 parts ether) is most effective, yielding a hard horny product that is very tough. The remaining solvent is removed from the grains by heating in vats under water, and the small amount of water remaining behind is removed by air drying. The solvent should be removed slowly in order to avoid warping of the grains. The British form their colloided double-base powder (cordite) by treating a high or 13 per cent nitrogen nitro-cellulose with a mixture of acetone and nitro-glycerine with some petroleum jelly. The nitro-glycerine increases the heat of burning of the powder and keeps the grains from becoming brittle.



For a flow sheet for nitrocellulose manufacture see Fig. 3

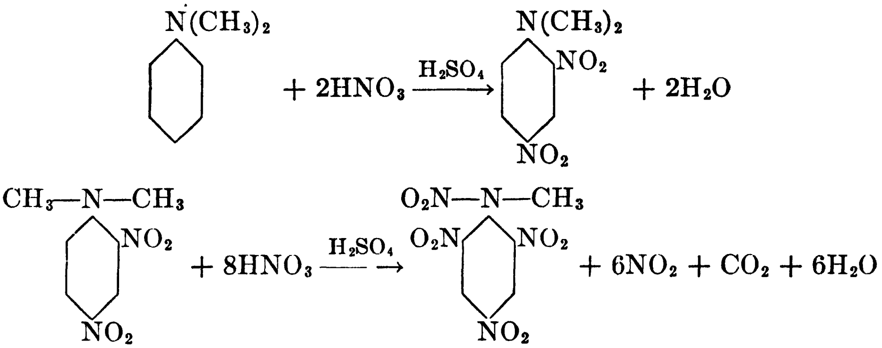
✱ **Note**: Asterisks denote equipment connected to solvent recovery system

FIG. 4.—Flow sheet for smokeless powder.

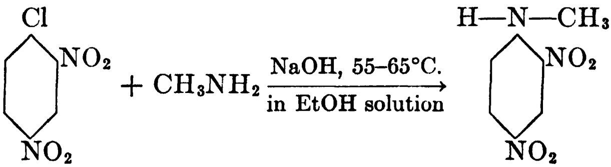


Trinitro-toluene.— Symmetrical trinitro-toluene is the most important military high explosive used in this country. Because of its low melting point (81°C.) it is loaded into shell in the molten state. It is superior to picric acid from the standpoint of safety by reason of its lower melting point and the fact that it has no tendency to form sensitive salts with metals. It is made by the nitration of toluene with mixed acids in cast-iron or steel nitrators. The nitration is performed in either one or three steps, the latter method being preferred in modern practice. The acids used are progressively stronger in each step of the nitration and the temperatures are progressively higher. After nitration, the unsymmetrical trinitro-toluenes and by-products are removed by agitation with a 5 per cent solution of sodium sulfite. After washing with warm water to remove all traces of impurities, the T.N.T. is dried by blowing with warm air, then flaked, and packed into paper-lined wooden boxes. Over-all yields are excellent.

Tetryl.—(2,4,6-trinitro-phenyl)-methylnitramine, $C_6H_2(NO_2)_3NCH_3NO_2$ is generally used as the base charge in blasting caps,[1] as the booster explosive in high-explosive shell, and as the sole bursting charge in certain aircraft cannon shell and antiaircraft shell. It is generally prepared by the action of mixed sulfuric and nitric acid on dimethylaniline in a multiple-stage nitration. The dimethylaniline may be first dissolved in sulfuric acid.



It may also be made by alkylating 2,4-dinitro-chloro-benzene with methylamine, then nitrating. This method is calculated to be more economical of raw materials, but the extreme toxicity of the dinitro-chloro-benzene weighs heavily against it. Tetryl is an extremely powerful high explosive with great shattering power.



$$C_6H_3(NO_2)_2\cdot NHCH_3 + \begin{Bmatrix} HNO_3 \\ H_2SO_4 \end{Bmatrix} = \text{tetryl}$$

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[1] Blasting caps are small metal capsules containing sufficient explosive to ensure the detonation of dynamite. In earlier days they were loaded with mercury fulminate or fulminate-$KClO_3$ mixtures. Many are now loaded with a small charge of fulminate or azide designed to set off a larger charge of tetryl which in turn sets off the dynamite.

Picric Acid.—Picric acid is not made directly by the nitration of phenol because too many oxidation by-products are formed. It is manufactured instead by the nitration of mixed phenol-sulfonates. The phenol-sulfonates result from heating 1 mole of phenol with 3½ moles of 66°Bé. sulfuric acid and holding the well-mixed mass at a temperature of 80°C. for about 4 hr. The phenol-sulfonates (mixed mono and di) are then run into nitrators constructed of acidproof brick. The nitration is carried out with mixed sulfuric and nitric acids.[1] After the addition of all the acid, the temperature is held at 100°C. for at least 1 hr.

Ammonium Picrate.—Ammonium picrate[2] is made by the neutralization of a hot aqueous solution of picric acid with ammonia water. It is employed for armor-piercing shell.

P.E.T.N.—Pentaerythritol tetranitrate, $C(CH_2ONO_2)_4$, may be made by the nitration of pentaerythritol with strong nitric acid, 94 per cent HNO_3, at about 50°C. The polyhydric alcohol is made by treating acetaldehyde with formaldehyde in the presence of lime. The lime leaves the reaction as calcium formate. Three aldol condensations occur followed by a cross-Cannizzaro reaction yielding $C(CH_2OH)_4$. It should not be confused with erythritol. The reactions follow:

$$3CH_2O + CH_3CHO \rightarrow (CH_2OH)_3CCHO \qquad (1)$$
$$(CH_2OH)_3CCHO + CH_2O + H_2O \rightarrow C(CH_2OH)_4 + HCOOH \qquad (2)$$
$$C(CH_2OH)_4 + 4HNO_3 \rightarrow C(CH_2ONO_2)_4 + 4H_2O \qquad (3)$$

P.E.T.N., an extremely powerful and sensitive explosive, has been used as a booster. Mixtures of T.N.T. and P.E.T.N. have been suggested for use where an extremely powerful bursting charge is wanted. It is probable that the reaction of decomposition may be expressed:

$$C(CH_2ONO_2)_4 \rightarrow 3CO_2 + 2CO + 4H_2O + 2N_2$$

Cyclonite.[3]—Cyclonite or symmetrical trimethylene-trinitramine, sometimes called *hexogen* or R.D.X., is a very interesting new booster and high explosive which is one of the most powerful explosives known at the present time. It is made by the destructive nitration of hexamethylene-tetramine with concentrated nitric acid. The reactions may be represented:

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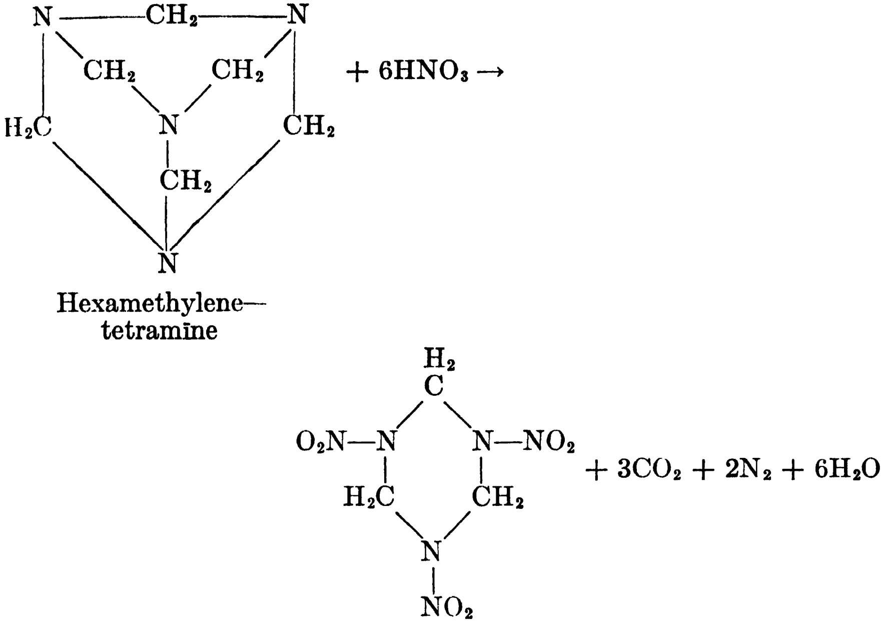
[1] Formerly strong nitric acid alone was used. Mixed acids cut down the health hazard caused by fuming, reduce the amount of acid required, and increase the yield of desired products. The use of mixed acid is now almost universal.

[2] Gerber, Ammonium Picrate Production for Military Explosive Requirements, *Chem. & Met. Eng.*, **51**, No. 3, 100 (1944), flow sheet from dinitro-chloro-benzene.

[3] Hale, *J. Am. Chem. Soc.*, **47**, 3754–3763 (1925).

$$6CH_2O + 4NH_3 \rightarrow (CH_2)_6N_4 + 6H_2O$$



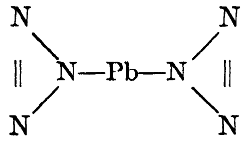
Hexamethylene-tetramine

Cyclonite

The nitric acid used is the fuming 95 per cent HNO_3 and must be water white. The cost of cyclonite is at present excessive, but it has many excellent properties and is capable of withstanding long storage.

Mercury Fulminate.—$Hg(ONC)_2$ has for many years been the most important initiating or primary explosive because of its excellent explosive properties and the ease with which it can be prepared. It is readily made by reacting a mixture of nitric acid and mercuric nitrate with ethyl alcohol. The steps involved in the reaction are very complicated and are not readily shown by a simple chemical equation. Commercially, the reaction is usually run on a small scale in glass carboys, only 1 lb. of mercury being used per carboy. The mercury is added to the carboys which are immersed in running water for temperature control. The nitric acid is added and the mixture allowed to set overnight. On the following morning the ethyl alcohol is added. The reaction is complete at the end of about 1 hr., and the mercury fulminate is removed by filtration. Mercury fulminate is stored under water for, when thoroughly wet, it is difficult to cause its explosion.

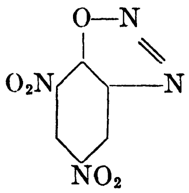
Lead Azide.—$Pb(N{=}N{\equiv}N)_2$ is another initiating explosive which has considerable use as the primary detonating explosive used in blasting caps. The formula of these triazo compounds is in doubt. Lead azide may have the structure: Because of the fact that it will react with brass to form the extremely sensitive copper azide, it is necessary that caps loaded with it be made of aluminum. Lead azide is manufactured by treating sodium azide with lead acetate or nitrate. Sodium azide may be made by treating sodium amide with nitrous oxide.



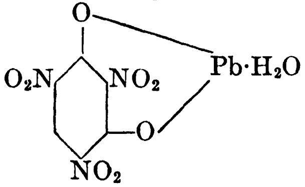
$$NaNH_2 + N_2O \rightarrow NaN_3 + H_2O;\ NaNH_2 + H_2O \rightarrow NaOH + NH_3$$
$$2NaN_3 + Pb(C_2H_3O_2)_2 \rightarrow Pb(N_3)_2 + 2Na(C_2H_3O_2)$$

Silver azide has also been used to a very limited extent.

Dinol.—Diazodinitro-phenol or 4,6-dinitro-benzene-1,2-diazooxide, was the first diazo compound ever discovered (Griess, 1858). Its valuable properties as a primary explosive were not generally recognized until recent years. It is made by diazotizing picramic acid. An internal coupling yields the product desired.



Lead Styphnate.—Normal lead trinitro-resorcinate is a comparatively new initiating explosive which is being quite widely used in the primers for sporting arms.



INDUSTRIAL EXPLOSIVES

For blasting purposes large quantities of *black powder* are still used. Black powder is an intimate mixture of KNO_3, charcoal, and sulfur, usually in the approximate proportions 75-15-10. For cheap blasting explosives the less desirable $NaNO_3$ is frequently substituted for KNO_3. $NaNO_3$ is less desirable because of its tendency to absorb water from the air. Thorough mixing is essential for good black powder; consequently,

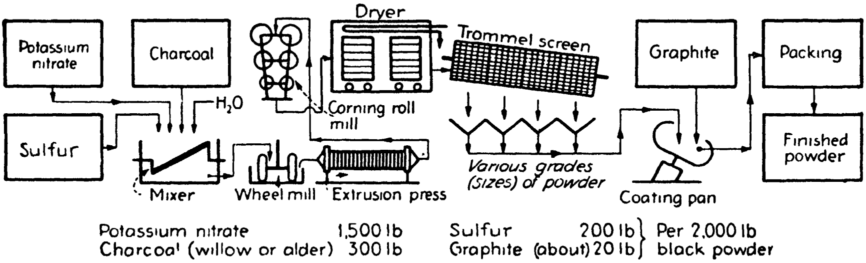
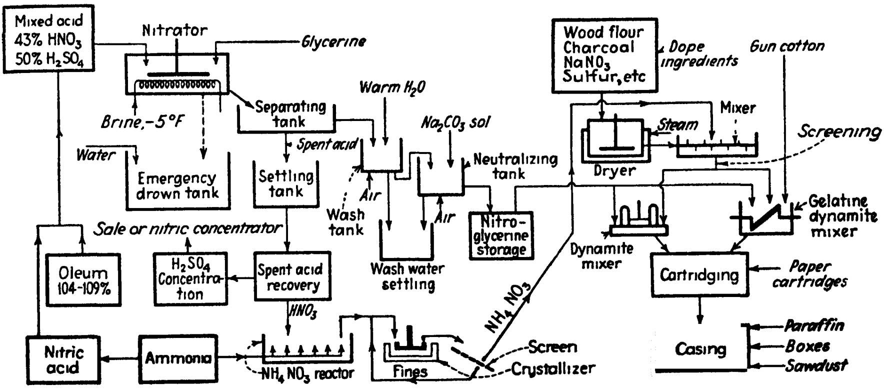


FIG. 5.—Flow sheet for manufacture of black powder.

it is customary to work the mixed raw materials under a wheel mill, as is depicted in Fig. 5. Certain observers think that this operation colloids the sulfur and produces a more homogeneous product than would be otherwise obtainable.

Black powder is relatively undesirable for use in mines because of the persistent flame produced on explosion and the ability of this flame to ignite gas and coal-dust mixtures. The fact that considerable quantities of carbon monoxide are evolved on its explosion is also a disadvantage. It remains in use principally because of its cheapness and because of the fact that it is not shattering in its action (very desirable in coal mining). The fact that the properties of black powder can be varied over quite wide ranges by altering the composition and the granulation has also been a deterrent to its replacement by other explosives.



HNO_3 (100%)	2,000 lb (10% recovered)	Refrigeration	1 5 tons ice equivalent	Per ton of nitroglycerine
H_2SO_4 (100%)	2,000 lb (96% recovered)	Direct labor	4 5 man-hr	
Glycerine	860 lb			

FIG. 6.—Flow sheet for nitro-glycerine and dynamites. Usually an evaporator is needed between the ammonium nitrate reactor and the crystallizer.

Black powder upon explosion liberates from each gram 718 cal. and about 270 cc. of permanent gases, but about 50 per cent of the products are solids. Among these products are CO_2, CO, N_2, H_2S, H_2, K_2CO_3, K_2SO_4, K_2S, and unreacted constituents.

Nitro-glycerine and Dynamite.[1]—Nitro-glycerine was the first high explosive to be employed on a large scale. The nitration is effected by slowly adding glycerine of high purity (99.9+ per cent) to mixed acid having the approximate composition: H_2SO_4, 50 per cent; HNO_3, 50 per cent. The nitration is accomplished in from 60 to 90 min. in agitated nitrators equipped with cooling coils carrying brine at −5°C. to maintain

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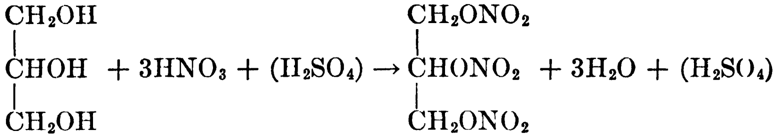
[1] *Cf.* GROGGINS, "Unit Processes in Organic Synthesis," p. 583, McGraw-Hill Book Company, Inc., New York, 1938; NAOUM (Symmes, *translator*), "Nitroglycerine and Nitroglycerine Explosives," The Williams & Wilkins Company, Baltimore, 1928.

a temperature below 15°C. Above this temperature there is great danger that the charge will begin to react very violently, ultimately resulting in explosion. After nitration, the mixture of nitro-glycerine and spent acid is allowed to flow through a trough (a trough is easier to clean completely than a pipe) into separating and settling tanks at some distance from the nitrator. Here the nitro-glycerine, being lighter than the spent acid, rises to the top. The nitro-glycerine is carefully separated from the acid and sent to the wash tank where it is washed twice with warm water. After these, it is treated with a 1 per cent sodium carbonate solution to ensure complete removal of any remaining acid. Additional washes with warm water are continued until there remains no trace of alkalinity. After this the material is well settled and sent to storage. The sequences of the *unit operations* and the *unit processes* involved in manufacturing nitro-glycerine and dynamite are shown in Fig. 6, where also the quantities of raw material are listed.[1] The product is really glyceryl trinitrate and the reaction falls under the (nitrate) esterification classification. The reaction may be formulated:



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3HNO_3 + (H_2SO_4) \rightarrow \begin{array}{l} CH_2ONO_2 \\ | \\ CHONO_2 \\ | \\ CH_2ONO_2 \end{array} + 3H_2O + (H_2SO_4)$$

Nitro-glycerine is a liquid very similar in appearance to the original glycerine. It is quite sensitive to blows and freezes at 56°F.; when solid it is less sensitive. As it has a strong tendency in this state to explode only partly, frozen nitro-glycerine must always be thawed before using.

To make nitro-glycerine easier and safer to handle it is usually manufactured into dynamite. The original dynamite was made by absorbing nitro-glycerine in kieselguhr. Such a mixture is easy to handle and can be made to contain as much as 75 per cent nitro-glycerine and yet retain its solid form. Nitro-glycerine in such mixtures, however, still freezes at comparatively high temperatures, and dynamite when frozen is relatively insensitive and may not detonate completely when set off. It is quite hazardous to thaw out dynamite rapidly. Because of the demand for a nonfreezing dynamite for work in cold weather, several dynamites containing other material designed to lower the freezing point of the nitro-glycerine have been put on the market. The material most widely used to lower the freezing point of dynamite is ethylene glycol dinitrate. This material is an excellent explosive in its own right. Such nonfreezing dynamites have potentials almost as great as "straight" dynamite.

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[1] Further details are available in the literature, recently in Chap. 32 of "Rogers' Manual of Industrial Chemistry," C. C. Furnas, editor, 6th ed., D. Van Nostrand Company, Inc., New York, 1942.

Kieselguhr dynamites are rarely used at present because they contain at least 25 per cent of inert material which greatly lowers their power per unit of weight. Modern dynamites generally use wood flour, ammonium nitrate, or sodium nitrate as the agent employed to absorb the nitro-glycerine. These materials, particularly ammonium nitrate, add appreciably to the efficiency of the explosion. Nitro-cellulose can be gelatinized by nitro-glycerine, and the resulting firm jelly is an exceptionally powerful high explosive commonly known as *gelatine dynamite.*

A wide variety of other explosives have been suggested for both commercial and military use, but most of these have been abandoned because of such properties as poor stability on storage, excessive cost of manufacture, tendency to form very sensitive materials on decomposition, and toxicity. The following materials have been important in the past or enjoy a limited use today: hexanitro-mannite, tetranitro-aniline, starch nitrate, hexanitro-diphenylamine, trinitro-benzene, etc.

Toxicity.—Almost without exception the nitro compounds and nitric acid esters used as explosives are toxic. The degree of toxicity varies widely with the material in question, but most are capable of causing acute distress if taken orally. Some materials used in the past have been extremely toxic; hexanitro-diphenylamine, for example, is an active vesicant. Extremely toxic properties would weigh heavily against any new explosive that might be introduced.

CHEMICAL WARFARE

The field of chemical warfare is generally taken to include those substances which by their chemical action produce powerful physiological effects, screening smokes, or incendiary action. Although it is currently assumed that the employment of such chemicals began with the First World War, the fact is that incendiary and asphyxiating substances have been used over the centuries in warfare, but they only reached a really effective stage on Apr. 22, 1915, with the release by the Germans of 600,000 lb. of chlorine along a 2-mile front against an unprotected enemy.

Toxic Materials.—The use of the so-called *poison gases* in warfare is a widely misunderstood and much maligned subject, the major cause of the misunderstanding being unreasoning fear and a lack of knowledge of the physical difficulties incident to establishing high concentrations of casualty-producing[1] agents over wide areas. Sensational reports have appeared in various newspapers claiming the discovery of new and terrible toxic agents capable of "wiping out an entire city without warning." These reports have no counterpart in fact. Briefly stated, although many proposed new, casualty-producing chemical agents have been studied, there is little likelihood that any are available that could cause the damage popularly believed probable. The requirements which a satisfactory chemical warfare agent must meet are so rigid that only a small group of compounds possess the necessary properties. Among the more important of these requirements are

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[1] It should be clearly understood that, in a military sense, a casualty is a disabled person, one who cannot fight. Casualties include both the wounded and the killed.

1. Volatility should be high enough to allow ready dispersal at temperatures met in both summer and winter warfare, and the material should be readily liquefiable so that it may be loaded into shell and bombs in the liquid state.
2. Stability should be sufficient to withstand storage.
3. The chemical should not readily react with or be decomposed by water, metals, or earth.

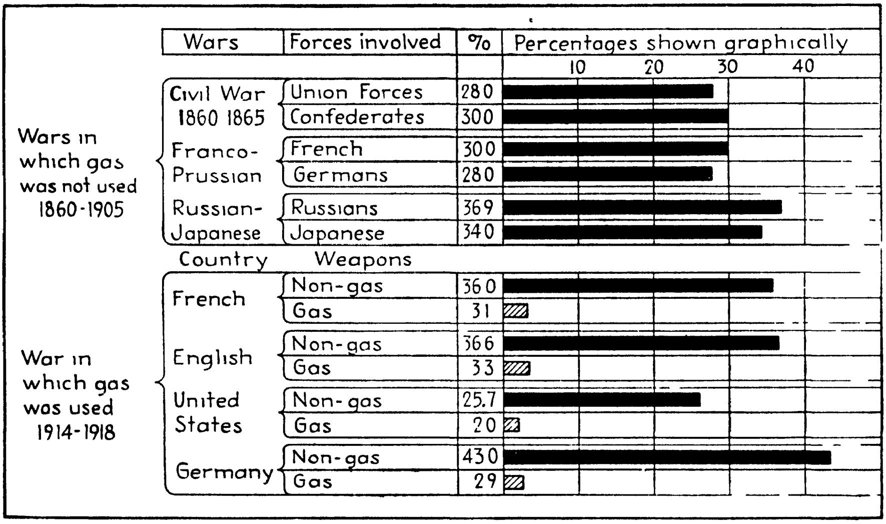

FIG. 7.—Mortality from gas wounds and from wounds produced by nongas in the First World War. (*From Gilchrist, World War Casualties, Chemical Warfare School Edgewood Arsenal, Md.*, 1928.)

4. The chemical should not be decomposed by the shock of explosion.
5. The chemical should be very toxic in small concentrations and should be difficult to protect against.
6. The chemical should be cheap and easy to manufacture from readily available raw materials in enormous quantities without the use of too highly specialized equipment. It is preferable that the toxic properties develop only in the last stages of manufacture.

Contrary to popular opinion, from a military standpoint, it may be undesirable to cause the death of the personnel of the enemy. Deceased personnel may be disposed of in a very short time; incapacitated personnel require the attendance of approximately four persons during the time of their hospitalization. The services of five persons are hence of no military value during this time. In casualty-producing effect the chemical agents have no peer, but they produce a very low percentage of fatalities, as shown by Fig. 7, wherein are charted the comparative disabilities and mortalities caused by gas and other weapons in various wars. The ratio of the mortality percentages shows the relative chances for recovery of those wounded by gas or other weapons and demonstrates that a man injured by gas had a 12 to 1 better chance for recovery than one wounded by other means. Table 3 shows the permanent disabilities among those recovering. A persistent rumor that aftereffects of chemical warfare (tuberculosis, etc.) cause an exceptionally high mortality rate in later years has been disproved.[1] It should never be forgotten that to apply any warfare agent effectively there is always great wastage of material. For example, Kibler[2] states for the First World War, "Casualty records show that for each casualty there were required 23 mustard shells or 60 lb. of mustard, 100 high-explosive shells or 500 lb. of high explosives, or 5,000 rounds of rifle ammunition."

TABLE 3.—SHOWING PERMANENT DISABILITIES RESULTING FROM WAR WOUNDS IN EX-SOLDIERS AND THE WEAPONS RESPONSIBLE,[a] 1917–1918

Nature of deformity	Total number	Weapons responsible	
		Gas	Others
Loss of 1 or more limbs	4,403	0	4,403
Loss of 1 or more joints	4,790	0	4,790
Loss of sight, right eye	307	16	291
Loss of sight, left eye	289	10	279
Loss of sight, both eyes	44	4	40
Loss of sight, eye, unknown	139	3	136
Totals	9,972	33	9,939

[a] GILCHRIST, "World War Casualties," Chemical Warfare School, Edgewood Arsenal, Md., 1928.

Based on physiological action the chemical agents may be classified as follows and as arranged in Table 4:

1. Lachrymators or tear gases, which produce temporary inability to see.
2. Sternutators,[3] which cause sneezing, nausea, and temporary physical disability.

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[1] KOONTZ, War Gases and Tuberculosis, *Arch. Internal Med.*, **39,** 833–864 (1927).

[2] From an address by A. L. Kibler, Chief of the Information Division of the Chemical Warfare Service, U.S. Army, given Sept. 11, 1940, at the American Chemical Society meeting at Detroit, Mich., before the Division of Industrial and Engineering Chemistry.

[3] JACKSON, Sternutators, *Chem. Rev.*, **17,** 251–292 (1935).

3. Lung injurants, which, in case of severe contact, cause death from edema of the lungs.

4. Vesicants or blister-producing agents, which act mostly on the skin but also on any part of the body contacted. The effect may be very serious.

The sternutators listed in Table 4 are solids at ordinary temperatures and are dispersed as fine smokes. A modern gas mask gives complete protection against the lethal effects of all of these. For protection against the vesicants, however, somewhat uncomfortable protective clothing must be worn. Vesicants, therefore, have the highest nuisance value.

TABLE 4.—CHARACTERISTICS OF IMPORTANT CHEMICAL WARFARE AGENTS

Agent	Formula	Symbol	Boiling point, °C.	Odor	Persistency
Lachrymators or tear gases:					
Chloro-acetophenone	$C_6H_5COCH_2Cl$	CN	247	Apple blossoms	Solid for days; burning mixture 10 min.
Bromo-benzyl cyanide	$C_6H_5CHBrCN$	CA, BBC	225	Sour fruit	Few days to several weeks
Sternutators or vomiting gases:					
Diphenylamine-chloro-arsine or Adamsite	$NH(C_6H_4)_2AsCl$	DM	410[a]	Not pronounced (moldy hay)	10 min.
Diphenyl-chloro-arsine	$(C_6H_5)_2AsCl$	DA	383	Not pronounced (shoe polish)	5–10 min.
Lung injurants or choking gases:					
Chlorine	Cl_2	CL	−34.6	Pungent	1–5 min.
Phosgene	$COCl_2$	CG	8.3	Ensilage	1–10 min.
Diphosgene	$ClCOOCCl_3$	DP	127	Ensilage	30 min.
Chloropicrin[b]	CCl_3NO_2	PS	112	Fly paper	1 hr. to 1 day
Vesicants or blister gases[c]:					
Mustard	$(ClCH_2CH_2)_2S$	HS, H	228	Mustard	1 day to weeks
Lewisite	$ClCH{\cdot}CHAsCl_2$	M1, L	190	Geranium	1 day to 1 week
Nitrogen mustards	....	HN	......	Slightly fishy or none	Less persistent than mustard

[a] Decomposes; melting point 195°C.

[b] Also causes vomiting and has some lachrymatory action. A much more extensive and detailed tabulation of these and other war chemicals is given opposite p. 262 of Prentiss, "Chemicals in War," McGraw-Hill Book Company, Inc., New York, 1937.

[c] The term *gas* used by Chemical Warfare Service is a very broad one as many of the substances employed are liquids or solids at ordinary temperatures but give off toxic or irritating vapors or gases.

Mustard, bis(2-chloro-ethyl) sulfide, $(ClCH_2CH_2)_2S$, is a heavy, oily liquid which freezes at 14.4°C. It has very little odor in the pure state but the technical material smells strongly of mustard or horseradish. It is made by bubbling dry ethylene into sulfur monochloride at approximately 30°C., some mustard from a previous batch being present. A lead-lined steel reactor is employed with a refrigerating liquid in lead coils.

$$S_2Cl_2 + 2CH_2{:}CH_2 \rightarrow (ClCH_2CH_2)_2S + S$$

The sulfur remains in colloidal suspension and is only partly removed as it has little effect on the physiological effect of the mustard. After the mustard is made, it is allowed to settle for a while to permit some sulfur and other solids to settle out. The resultant oil is a light brownish material.

The sulfur monochloride is made by passing dry chlorine gas into steel tanks containing melted sulfur, $2S + Cl_2 \rightarrow S_2Cl_2$. Once started, the reaction evolves heat and the tanks must be cooled by a water spray. During the First World War the ethylene was prepared by the dehydration of ethyl alcohol in the vapor phase using Al_2O_3 or kaolin as a catalyst, but now large amounts are available from the gas from cracking stills in the petroleum industry. Ethylene can also be made readily by dehydrogenating ethane. Thus enormous amounts could be made, particularly in the United States, from easily available raw materials.

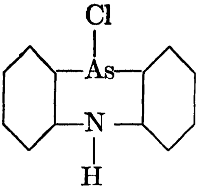
As mustard is readily absorbed by rubber and leather, special protective clothing is required. Mustard acts in three ways: as a lachrymator in lowest effective concentration, as a lung irritant at slightly higher concentration (0.007 mg. per l.), and as a vesicant or burning agent at enhanced concentrations either as a vapor or as a liquid.

Lewisite, β-chlorovinyl-dichloro-arsine, $ClCH{=}CHAsCl_2$, was named for its discoverer, Prof. W. Lee Lewis, who was active as a research officer with the U.S. Chemical Warfare Service during the First World War. Lewisite results when acetylene is passed through arsenic trichloride in the presence of anhydrous aluminum chloride. The temperature should not be allowed to exceed 50°C. The aluminum chloride is removed by washing with hydrochloric acid and the Lewisite distilled out under vacuum. As side reactions bis(β-chlorovinyl)chloro-arsine and tris(β-chlorovinyl)arsine are formed. These may be converted to Lewisite by heating with arsenic trichloride. Lewisite has strong vesicant properties and is also a powerful systemic poison. Because of its high cost and the unavailability of large quantities of arsenic, it will probably not replace mustard.

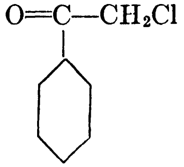
Phosgene, carbonyl chloride, $COCl_2$, is made by the union of carbon monoxide and chlorine in the presence of a catalyst, usually carbon granules.

$$CO + Cl_2 \rightarrow COCl_2$$

As much heat is evolved, the reaction is usually started in a reactor which is water-cooled and completed in a similar reactor in which the temperature is allowed to rise slightly. This material is extremely toxic but its persistency is low. It reacts readily with sodium phenate or hexamethylene-tetramine which render it nonpoisonous. *Much of this material is used during peacetime for organic syntheses, particularly for the manufacture of acetyl chloride and Michler's ketone. It must be* loaded into shell at very low temperatures.



Adamsite, diphenylamine-chloro-arsine, is a canary-yellow crystalline solid named after Prof. Roger Adams. This agent is dispersed in the form of a smoke. It has been used during peacetime for dispelling persistent mobs. Adamsite causes acute nausea which persists for some time but leaves no ill effects. It is prepared by the reaction of diphenylamine with arsenic trichloride.



Chloro-acetophenone, phenyl-chloromethyl ketone, is a very effective lachrymator produced from benzene and chloro-acetyl chloride. It is more desirable than bromo-benzyl cyanide for general use because of its greater stability and its lesser tendency to corrode metals. For military use it is generally applied in solution with other agents. Two such representative solutions are (1) chloro-acetophenone, 23.2 per cent; chloropicrin, CCl_3NO_2, 38.4 per cent; and chloroform, 38.4 per cent; (2) chloro-acetophenone, 10 per cent; carbon tetrachloride, 45 per cent; and benzene, 45 per cent. It is widely used for training in chemical warfare work and in protection against prowlers, etc.

Screening Smokes.—A variety of chemical materials have been employed for the purpose of producing smokes[1] or fogs primarily designed to conceal the movements of troops or machines from the enemy. A great deal of the hiding effect of the agents used is due to their great deliquescence which enables them to absorb water from the air and form small droplets which scatter the light rays. This is more effective than to obstruct. Smokes may be dispersed by various methods, mechanical, thermal, and chemical.

Titanium tetrachloride is dispersed by spraying from airplanes or atomized by explosion in mid-air. When exposed to air it hydrolyzes.

$$TiCl_4 + 4H_2O \rightarrow Ti(OH)_4 + 4HCl$$

The hydroxide and the hydrochloric acid are deliquescent and aid in forming the smoke. It is very important that all apparatus used with this material be kept dry, for the $Ti(OH)_4$ is a solid and will clog any passages. $TiCl_4$ is relatively high in cost, and the supply of titanium ore available is distinctly limited.

Sulfur trioxide-chlorosulfonic acid mixtures are extremely low in cost compared with $TiCl_4$ and are quite as effective in producing smoke. The most efficient mixture has been found to consist of SO_3, 55 per cent; $ClSO_3H$, 45 per cent. The constituents hydrolyze in air, thus

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[1] JACKSON, Smoke Forming Chemicals, *Chem. Rev.*, **25**, 67 (1939).

$$SO_3 + H_2O \rightarrow H_2SO_4$$
$$ClSO_3H + H_2O \rightarrow H_2SO_4 + HCl$$

All these hydrolysis products are deliquescent and enlarge their particle size by further water absorption. The smoke is irritating and corrosive but harmless.

White phosphorus is loaded directly into shell, bombs, and grenades. The material is dissipated by the force of the explosion and immediately burns to P_2O_5 which absorbs water from the air. P_2O_5 has the greatest obscuring power of any known smoke-producing material. The smoke will cause coughing but is harmless. There is danger of injury from the burning white phosphorus particles which produce burns that are very slow to heal. These particles also have some incendiary effect.

Zinc-containing Mixtures.—The principal components of this type of smoke are powdered zinc and chlorine-containing materials, *e.g.*, carbon tetrachloride or hexachloro-ethane. Such materials react with the zinc to produce $ZnCl_2$ which is very hygroscopic.

$$3Zn + CCl_3CCl_3 \rightarrow 3ZnCl_2 + 2C$$

Ammonium perchlorate, NH_4ClO_4, is added to oxidize the carbon and keep the reaction going. There is also added ammonium chloride to control the burning rate and a small amount of calcium carbonate to stabilize the mixture. The material is set to burning by a small amount of an igniting mixture, *e.g.*, a modified black powder. These mixtures are dissipated by means of pots or so-called *candles.*

Incendiaries.[1]—The incendiary bomb to be dropped from airplanes is proving to be very effective in the present war. The small bomb weighing approximately 2½ lb. has been widely employed. Its body is usually made of a combustible magnesium alloy (elektron metal). The filler, which may be a mixture of barium nitrate and some aluminum with four-fifths thermite, is used to ignite the case. Thermite is a mixture of aluminum powder and iron oxide. When ignited, it burns fiercely at a high temperature and *cannot be extinguished by means of water.*

$$3Fe_3O_4 + 8Al \rightarrow 4Al_2O_3 + 9Fe; \qquad \Delta H = -719{,}000 \text{ cal.}$$

Some readily ignitable material, such as black powder, is used to ignite the thermite. White phosphorus is occasionally employed in incendiary bombs but is not so effective. Many incendiary bombs contain jellied petroleum oils to enlarge their sphere of burning and effectiveness. In this type of incendiary, the required oxygen is supplied by the air when and where the ignition takes place.

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[1] GILL, Incendiary Bombs, Basic Principles, *Pharm. J.*, **139**, 447 (1937); ANON., Recent Developments in Incendiaries, *J. Chem. Education*, **20**, 59 (1943); PRENTISS, "Chemicals in War," Chap. 12, McGraw-Hill Book Company, Inc., New York, 1937; DEPPLER, Thermite—Its Use in War and Industry, *Chem. & Met. Eng.*, **49**, No. 7, 92 (1942).

Protective Devices.—The present gas mask is a marvel of efficiency and an increase in comfort. It protects the wearer not only against known gases but also against probable new ones. The major constituent employed in it is activated carbon. This material possesses the faculty of adsorbing high-molecular-weight vapors without regard to chemical structure. Since the probable low-molecular-weight materials have been studied thoroughly and additional materials for their destruction are present, any new material probably would be of high molecular weight and would be adsorbed by the activated carbon.

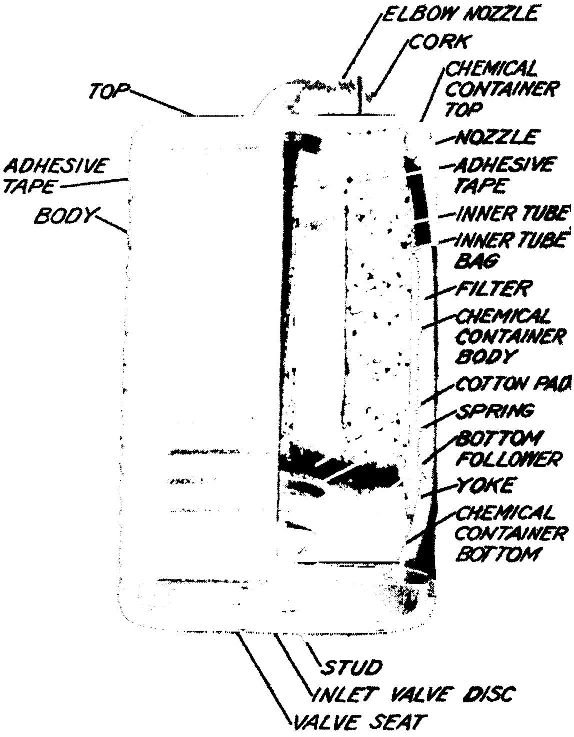

FIG. 8.—A sectionalized modern American canister

Activated carbon is made by carbonizing certain woods,[1] then increasing their adsorptive capacity by a process of partial oxidation and steam distillation. This is usually done by heating the charcoal in the absence of air to a high temperature (about 900°C.) and blowing with superheated steam. This charcoal is broken into lumps and carefully screened to size. All dust is removed since dust would plug the canister and make breathing difficult.

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[1] Most desirable woods are (1) coconut hulls, (2) fruit pits, and (3) hardwoods. Probably in the near future there will be available activated carbons for masks derived from materials other than wood. See Chap. IX on Industrial Carbon.

Soda lime granules are also present in the mask canister. The material used in making these granules usually consists of a mixture of $Ca(OH)_2$, portland cement, NaOH, $NaMnO_4$, and kieselguhr. In the presence of water vapor, the activated carbon catalytically decomposes phosgene almost instantaneously.

$$COCl_2 + H_2O \rightarrow CO_2 + 2HCl$$

The soda lime is intended to absorb the HCl thus produced. The $NaMnO_4$ oxidizes poisonous arsenicals. In order to remove irritant smokes a *filter* of cotton or wood fiber is incorporated. This modern gas mask, the canister of which is reproduced in Fig. 8, is a remarkably efficient device. Its constituents act as removal agents in the following manner:[1]

Chlorine by activated carbon + soda lime.
Phosgene (and hydrolysis products) by activated carbon + soda lime.
Chloropicrin by activated carbon.
Mustard by activated carbon.
Chloro-acetophenone by filter + activated carbon.
Bromo-benzyl cyanide by activated carbon.
Diphenyl-chloro-arsine by filter.
Diphenylamine-chloro-arsine by filter and permanganate.
Lewisite (and other arsine derivatives) by permanganate + carbon + soda lime.

Against the vesicants there are at present no really adequate means of defense except special protective clothing designed to cover the entire body. The best defense against these materials is, therefore, a known ability to produce them and disperse them more rapidly than the enemy, *i.e.*, a good offense.

Peacetime Use of Irritating Chemicals.—To control mobs without resorting to firearms, the use of chemical warfare agents is now standard practice. The desired effect is attained by making the members of any rioting group so uncomfortable that they lose their desire to fight. For this purpose is used chloro-acetophenone, CN, a powerful and instantaneous tear gas, or a mixture of this with diphenylamine-chloro-arsine (Adamsite or D.M.), a sickening gas or sternutator. The latter alone cannot be used effectively in riot work because it does not act at once, but its slightly delayed nausea is a powerful deterrent to rioting. Such lachrymators and sternutators are loaded[1] into short-range shell, grenades, or candles. They are generally dispersed by an explosion in the device with the active agent.

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[1] After Wood, The Chemistry of the Chemical Warfare Agents and of Protection against Them, *Military Surgeon*, **1928**, 322–338.

As a by-product[2] of the studies pursued by the Chemical Warfare Service of the U.S. Army, General Fries describes such peacetime activities as boll-weevil control, protection of marine piling from borers, ship-bottom paints, ship fumigation, control of mobs, protection against industrial poisons, and development of improved gas masks for factories and mines.

PYROTECHNICS

Because many states have passed rigid antifireworks laws, the pyrotechnics industry holds at present only a fraction of its former importance. Pyrotechnic mixtures, however, still have a number of fairly spectacular uses in our modern civilization: parachute flares enable airplanes to land safely on strange terrain, marine signal rockets have been much improved by attachment to parachutes, the old red signal flare (fusee) has become almost a requirement for a modern truck as well as for trains, and many pounds of colored light mixtures are being used for military purposes (tracer bullets and Very lights).

Pyrotechnic products, in general, consist of mixtures of strong oxidizing agents, easily oxidizable materials, and various other materials to act as binders and to alter the character of the flame, together with the color-producing chemical itself.

Parachute Flares.—A typical composition used in the manufacture of parachute flares contains the following materials for the purposes indicated: barium nitrate, oxidizing agent, 34 per cent; metallic magnesium, grained, to give heat, 36 per cent; aluminum powder, to give strong light, 8 per cent; sodium oxalate, to give a yellow tint to the light, 20 per cent; calcium stearate, castor oil, and linseed oil, as binders, 2 per cent.

Before mixing, the magnesium should be coated with linseed oil to prevent its oxidation on storage. As this formula does not fire readily, an igniter consisting of a mixture of 75 per cent black powder and 25 per cent of the above formula is always used to start the flame. The tug of the opening parachute actuates a mechanical device which starts the combustion of the formula. Parachutes are approximately 12 ft. in diameter and made of nylon or silk. A charge of approximately 10 lb. of the formula is used per flare.

Signal Flares or Rockets.—These are devices containing a pyrotechnic charge and a parachute to float the burning signal in the air.

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[1] For example, the Federal Laboratories of Pittsburgh, Pa., supply a full line of equipment, for such control, available to the police.

[2] FRIES, By-products of Chemical Warfare, *Ind. Eng. Chem.*, **20**, 1079 (1928).

These flares are usually shot into the air from a suitable pistol. The propelling charge is invariably black powder. Stars may be included if a colored fire is desired at the end of the flight. These stars are usually chlorate compositions with certain salts added to color the flames, *e.g.*, $Sr(NO_3)_2$ for red light, $BaCO_3$ or $Ba(NO_3)_2$ for green light, $Na_2C_2O_4$ for yellow light. For a nearly white light there is employed a properly proportioned mixture of the materials for red and green lights.

Truck Flares.—These are required in many states for use as warning lights in case of accidents or mechanical failures. These are slow-burning mixtures packed in paper tubes and ignited by means of scratch compositions on the head. A typical mixture is the following:

	Per Cent
$Sr(NO_3)_2$	68.3
Sulfur	13.0
Wood flour	0.5
$KClO_4$	7.8
Sawdust	10.4

When this mixture is tamped into a paper tube, it will burn at a rate of about 1 in. per min.

Tracer Compositions.—Tracer bullets contain in their base a light-producing material which makes their path of flight plainly visible to the shooter. Tracer compositions are usually mixed to give a red color. The following is typical: $Sr(NO_3)_2$, for red color and to act as oxidizing agent; magnesium metal, to supply heat; calomel, to sharpen the color; asphaltum, as a binder. As this composition does not ignite readily, it is capped with a small amount of an igniting mixture made of barium peroxide, BaO_2, magnesium, and asphalt. This mixture is ignited by the hot gases evolved by the propellant powder and in turn ignites the tracer composition.

MATCHES

The manufacture of matches is an essential industry. In this country it has become almost completely mechanized. At present, practically all matches fall within two classes: strike-anywhere matches and safety matches. Match-head compositions for *strike-anywhere matches* consist essentially of a material with a low kindling point, usually phosphorus sesquisulfide, P_4S_3, an oxidizing agent such as potassium or barium chlorate, ground glass, and glue. The P_4S_3 has completely displaced yellow phosphorus as the igniting material; many countries even forbid the use of yellow phosphorus. Because the use of yellow phosphorus has been eliminated in matches, the terrible bone disease, phossy jaw, is now practically unknown in the industry.

Safety matches owe their ignition to the generation of heat on the striking surface of the box, the coating of which consists mainly of red phosphorus, ground glass, and glue. No phosphorus sesquisulfide is used in safety matches, but antimony sulfide is used in the heads as a flame-producing agent.

In making matches, the wood sticks are formed by forcing wooden blocks through a steel die which carries the splints so formed through the next operations. They are then punched out. The sticks are first coated with paraffin, then dipped in the match composition, and allowed to dry.

PROBLEMS

1. The spent acid from a nitration process has the composition 43 per cent sulfuric acid, 36 per cent nitric acid, and 21 per cent water by weight. This acid is to be fortified by the addition of concentrated sulfuric acid containing 91 per cent H_2SO_4 and strong nitric acid containing 88 per cent HNO_3. The fortified mixed acid is to contain 40 per cent H_2SO_4 and 43 per cent HNO_3. Calculate the quantities of spent and concentrated acids that should be mixed together to yield 1,000 lb. of the desired acid.

2. Four hundred pounds of toluene is agitated with 4,000 lb. of mixed acid having the following composition: 7.5 per cent HNO_3, 80 per cent H_2SO_4, 12.5 per cent H_2O. If the nitration proceeds until all of the toluene is changed to mononitro-toluene, what will be the composition of the spent acid when the mononitro-toluene is separated from it?

3. Nitro-glycerine decomposes on explosion according to the following empirical formula:

$$C_3H_5(NO_3)_3 \rightarrow 3CO_2 + 2.5H_2O + 1.5N_2 + 0.25O_2$$

The temperature of the gases has been determined to be 3360°C. at the instant of explosion. If 5 grams of nitro-glycerine are exploded in a 1-l. bomb, what pressure should be exerted at the instant of explosion if the walls are assumed not to rupture?

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CHAPTER XXIII

THE PHOTOGRAPHIC INDUSTRY

The importance of photography to our modern civilization is a fact demanding no more proof than the simple statement that vision is the most common method that man has at his disposal for receiving and conveying impressions of the world in which he exists. There is no field of human activity at the present time, whether it be science, recreation, news reporting, printing, or the mere recording of family histories, which is not, in some phase or other, touched upon by the photographic process.

History.—The first recorded use of a lens for image formation occurred in the latter part of the sixteenth century. The effect of light on silver salts was known to the early alchemists, but it was Wedgwood, son of an English potter, at the beginning of the nineteenth century, who first successfully reproduced images, as negatives, on paper or leather impregnated with these silver salts. In 1819, Herschel discovered the fixing properties of sodium thiosulfate, thus paving the way for permanent pictorial reproductions and making possible the first exhibit, in 1839, of so-called *photographs*. The same year, the Frenchman, Daguerre, released to the public his formula for the manufacture of the familiar daguerreotype and the American, Draper, made what was probably the first photographic portrait.

The announcement of these processes created a demand for better lenses, which was soon satisfied. In 1850, Archer improved and perfected the "wet collodion" process, but in the hands of the public all the collodion processes eventually bowed to the superior gelatine dry plate discovered by Maddox. In 1888, George Eastman introduced transparent roll film and popularized the now familiar snapshot camera. Soon after this, Edison and Lumière invented practical methods for producing moving pictures.

Color-sensitized emulsions were used as early as 1904 by the Hoechst Dye Works of Germany, and the famous Wratten panchromatic plates were introduced in 1906. Velox developing-out paper was announced in America at about the same time, as the result of the discoveries of the late Dr. Leo H. Baekeland. Portrait film was introduced about 1920, and projection printing came into general use about the same time. Since the early twenties developments in all phases of the art have been fundamental and rapid, culminating with the introduction of natural color film about 1928 and practical amateur color prints in 1941. It is this latter field, color photography, that now holds the most promise for the future. The present advanced position of the photographic industry was attained as the result of thorough research on the fundamentals in this field and their application.

Uses and Economics.—The materials produced by the photographic industry have multitudinous applications in science, business, art, and recreation. In the year 1939 the 160 plants of this industry, together with their 17,200 wage earners, made the following products:[1]

Cameras	$ 17,346,000
Projectors	8,414,000
Film (not including X-ray)	55,492,000
Film, X-ray	10,237,000
Sensitized paper	15,821,000
Sensitized plates and slides	868,000
Photocopying paper (blueprint, etc.)	5,383,000
All other materials	12,951,000
Total, photographic materials and apparatus	$126,512,000

The 749 establishments producing lithographing and photo-lithographing materials manufactured products valued at $154,395,000 in 1939. Photoengraving plants produced $55,619,000 worth of products in 694 plants, and the photogravure and rotogravure plants, 24 in number, produced $18,615,000 worth of products and employed 2,623 wage earners.

Photographic Process. *Cameras.*—The essential parts of a camera include (1) a lightproof chamber, (2) a lens for forming the image, (3) a device for supporting the film or plate, (4) a shutter for controlling the quantity of light admitted, and (5) a view finder for determining the area being photographed. Two additional accessories, not absolutely necessary but extremely useful, are a focusing device and a diaphragm. All types of cameras have these parts and differ only in their degree of refinement and method of operation. They may be classified as box cameras, folding cameras, reflex cameras, plate and film-pack cameras, view and studio cameras, miniature cameras, and a group of special varieties which include stereo cameras, panoramic cameras, and recording cameras. In addition to the so-called *still* cameras, there are numerous varieties of motion-picture cameras.

Photographic Materials.—A review of materials used for recording the photographic image resolves itself quite logically into three parts: (1) a discussion of the various types of film or plate for the negative image —orthochromatic, panchromatic, infrared, and color, (2) a description of the different papers for the positive image—chloride, bromide, and chloro-bromide, and (3) a brief mention of so-called *transparencies.*

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[1] 1940 Census of Manufactures, U.S. Bureau of Census, Washington, D.C.

All *films* and *plates* consist essentially of an emulsion on a support of glass, cellulose nitrate, or cellulose acetate. The emulsion is composed of a suspension of minute silver halide crystals in gelatine, suitably sensitized by the addition of certain dyes or various classes of sulfur compounds. In addition, antifogging agents, hardening agents, and an antihalation backing are also used. The back of the film is generally coated with a layer of hardened gelatine to prevent curling.

Ordinary emulsions, to which no specially sensitizing material has been added, are sensitive only to blue and ultraviolet. Orthochromatic emulsions are sensitive to the above and also to green, while panchromatic emulsions are sensitive to all colors of the visible spectrum. The latter type may be further subdivided into type A, sensitive highly to blue and with much lower sensitivity to green and red; type B, or orthopanchromatic with a high green and blue sensitivity and a slightly lower red sensitivity; and type C, or hyperpanchromatic with a fairly high green sensitivity and an extremely high red sensitivity. Infrared emulsions, as their name implies, are sensitive beyond the visible spectrum and respond to wave lengths as long as 13,000 Å. Many organic dyes can be used as sensitizing compounds,[1] but the sensitizers most commonly used today belong to the cyanines, xanthenes, styryls, or the flavine series. These dyes are essentially transformers of energy, changing the light that they absorb into wave lengths that affect the photographic emulsion.

The support for most photographic papers[2] is a high-grade sulfite pulp, prepared in both single and double weights and coated with a layer of precipitated barium sulfate in hardened gelatine to present a smooth surface for the light-sensitive emulsion.

Lantern slides that have a glass support and motion-picture film, the base of which is either cellulose acetate or nitrate, both constitute the *transparencies* of the photographic industry. Naturally these have an emulsion coating.

Development and Fixing.[3]—Modern developing solutions contain mainly four functional constituents: an organic reducing agent, a preservative, an accelerator, and a restrainer. The function of the *reducing agent* is to reduce, chemically, the silver halide to metallic silver at the various points where light has produced the latent image. Chemically, they are polyhydroxy, aminohydroxy, or polyamine derivatives mostly of the aromatic series. Less than a dozen different chemicals are in common use today. These include pyrogallol or 1,2,3-trihydroxy-benzene, hydroquinone, or *p*-dihydroxy-benzene, Pictol or Metol or sulfate of N-methly-*p*-aminophenol, *p*-aminophenyl-glycine or Glycin, Eikonogen or sodium salt of 1-amino-2-naphthol-6-sulfonate, Amidol or the monohydrochloride of the 2,4-diamino-phenol, Rodinol or *p*-amino-phenol, and *p*-phenylene-diamine.

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[1] Kornfeld, The Action of Optical Sensitizers on the Photographic Plate. General summary with 90 references, *J. Phys. Chem.*, **42,** 795 (1938).

[2] Dutton, Types of Photographic Papers, *Am. Phot.*, **32,** 872–883 (1938); Wheeler, "Photographic Printing Processes," Chapman & Hall, Ltd., London, 1930.

[3] Rabinowitsch, The Mechanism of Development, *J. Phys.*, **5,** 232 (1934); "The Chemistry of Photography," Mallinckrodt Chemical Works, St. Louis, 1935; Crabtree and Matthews, "Photographic Chemicals and Solutions," American Photographic Publishing Company, Boston, 1939.

The *preservatives* guard the developer against aerial oxidation. The most common is sodium sulfite but the bisulfite and metabisulfite are also employed. The *accelerators* increase the alkalinity of the developing solution and hence increase the activity of most of the developing or reducing agents. They include the carbonates of sodium and potassium, sodium metaborate, and borax In order to control the speed of the alkalized developer it is necessary to employ a *restrainer*, usually potassium bromide. Other agents added to the developing solution in a limited way include various *hardeners* (formaldehyde or chrome alum), citric acid for *clarification*, methanol as a *solvent*, and various sugars to control the *rate of diffusion* of the developer into the emulsion.

The *theory*[1] of the development of the photographic image is connected with the properties of the emulsion. In the emulsion there are sensitive spots where Ag_2S molecules are present (*cf.* Emulsions, page 472). When a minute amount of light energy contacts these supersensitive molecules, a free atom of silver is liberated. These almost infinitesimal nuclei of silver constitute the latent image that is changed into the visible image by the developer depositing on these nuclei sufficient metallic silver from the silver haloids of the emulsion.

Modern *fixing agents*[2] are of the nonhardening or acid-hardening type. Their main purpose is to render the silver image permanent by dissolving away the undeveloped silver halide. In addition, the acid-hardening baths neutralize the alkali of the occluded developer and harden the emulsion. The latter type is most commonly employed and includes a silver halide solvent (sodium or ammonium thiosulfate), an antistaining agent (acetic or citric acid), a preservative (sodium sulfite), and a hardening agent (potassium chrome alum or formaldehyde).

The photographic process may be summarized by these steps: exposure of the negative film or plate in a camera followed by development of the latent image, fixing of the image by removal of the unaffected but still sensitive silver halides, and drying of the negative. The negative is used to make a positive usually on paper, which is subjected to the same sequences of development, fixation, and drying.

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[1] JAMES and KORNFELD, Reduction of Silver Halides and the Mechanism of Photographic Development, *Chem. Rev.*, **30**, 1–32 (1942), 153 references; MEES, "The Theory of the Photographic Process," The Macmillan Company, New York, 1942.

[2] WARWICK, The Laws of Fixation, *Am. Phot.*, **11**, 585 (1917).

Manufacture of Films, Plates, and Papers.—In the making of photographic films, plates, and papers three distinct steps are carried on: (1) the preparation of the light-sensitive emulsion, (2) the manufacture of the base or support for the emulsion, and (3) the coating of the emulsion on the base. The flow sheet shown in Fig. 1 gives a general representation of the manufacturing steps involved.

Emulsions.—The so-called photographic *emulsion* is in reality not a true emulsion but rather a dispersion of tiny silver halide crystals in gelatine[1] which serves as a mechanical binder, a protective colloid, and a sensitizer for the halide grains.

Many different types of silver halide emulsions are manufactured, the characteristics of each being dependent upon the silver halide used and the details of manufacture. In slow positive emulsions for photographic papers the bromide, chloride, and chloro-bromide are chosen. Chloro-bromide and pure bromide emulsions are also employed for lantern slides and other very slow plates. All fast emulsions, usually for negatives, contain silver bromide and small amounts of silver iodide. The iodide is essential for high-speed types but seldom exceeds 5 per cent. The finished emulsion generally consists of 35 to 40 per cent silver halide and 65 to 60 per cent gelatine.[2]

The manufacture of the emulsion may be divided into four principal steps: precipitation, first ripening, washing, and second or afterripening. The following presentation will deal with AgBr-AgI emulsion and is further illustrated by Fig. 1.

1. *Precipitation.*—The gelatine after soaking in cold water for about 20 min. is dissolved in hot water. The requisite quantities of KBr and KI are dissolved in this solution, which is then ready to receive the $AgNO_3$ solution. In the case of the ammonia process a 10 to 15 per cent excess of KBr is used and the amount of gelatine is 20 to 60 per cent of the total required in the finished emulsion. For neutral or "boiled" emulsions a 2 to 5 per cent excess of KBr is generally used and 10 to 20 per cent of the total gelatine.

In the ammonia process a silver nitrate solution is mixed with concentrated ammonia until the initial precipitate of Ag_2O redissolves. This solution is added slowly, with thorough mixing, to the halide-gelatine solution. The mixing temperature is usually about 40°C.; at 50°C. and higher, fog will appear.

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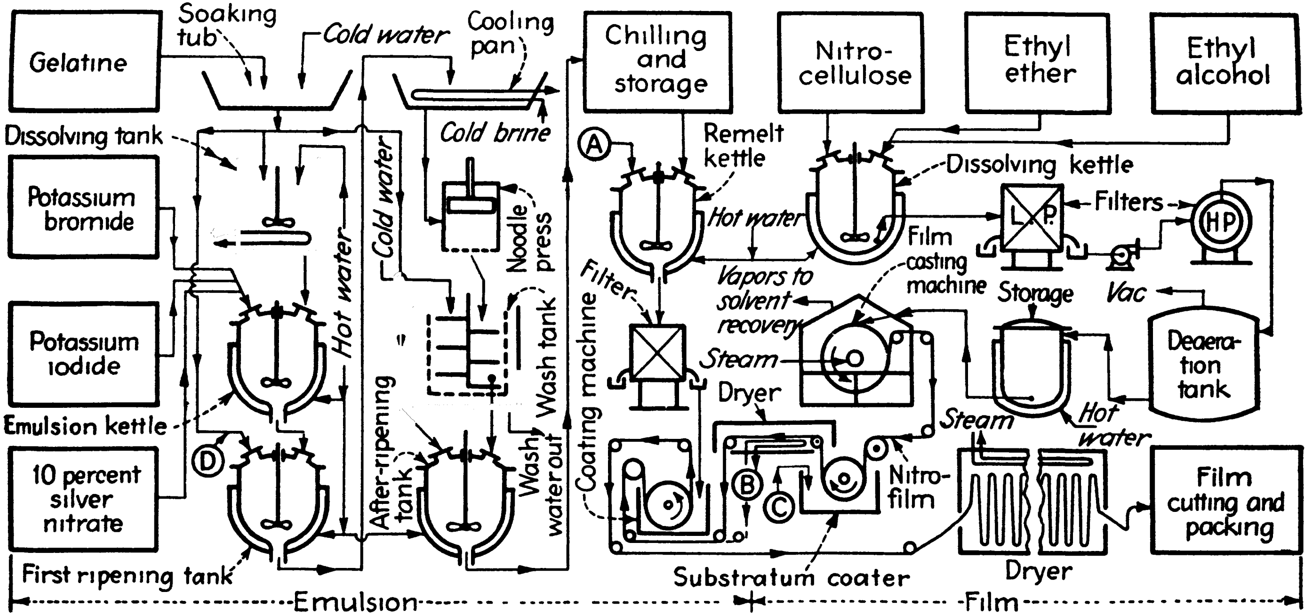
[1] See Chap. XXV.

[2] CARROLL, The Preparation of Photographic Emulsions, *J. Chem. Education*, **8**, 2341–2367 (1931).



Notes. Ⓐ Chrome alum, preservative, (phenol or thymol), saponin, KBr and sensitizing dyes added here. Ⓑ If special papers or acetate film base are being coated, they enter here Ⓒ Gelatine and solvent used for substratum coating Ⓓ Gelatine added at close of ripening period.

Potassium bromide	225 lb	Silver nitrate	20 lb	Ethyl alcohol	90 gal	Per 10,000 sq. ft. of film; solvents mostly recovered
Potassium iodide	06 lb.	Nitrocellulose	450 lb	Ethyl ether	180 gal	
Gelatine	800 lb.	Camphor	50 lb.	Amyl alcohol	3 gal.	

FIG. 1.—Flow sheet for making photographic film and paper

For neutral emulsions no ammonia is used. A 10 per cent silver nitrate solution is added to the halide-gelatine solution at 60 to 80°C.

In this mixing operation an excess of KBr is necessary to produce *large grain size and to prevent interaction of silver ions with the gelatine. The KBr solution is prepared with a relatively small part of the total* gelatine, as too much of the latter would interfere with grain growth during the ripening step. Moreover, the principal part of the gelatine is protected from the harmful influence of heat and ammonia. However, care should be taken that AgBr does not settle out owing to the smaller quantity of gelatine. Careful control of the mixing process is essential, as the concentrations of the solutions, the temperature, and the manner in which the $AgNO_3$ solution is added all have a pronounced effect on the character of the emulsion.

2. *First Ripening.*—The ripening or digesting process is essentially a continuation of grain growth under the influence of heat, the temperature being about the same as that of the mixing step. The excess of KBr in the emulsion increases the solvent capacity for AgBr. The small crystals, being more soluble than the large ones, tend to dissolve and reprecipitate upon the large crystals.[1] Since the sensitivity of the final product is dependent upon the grain size, the ripening step is an important one and warrants careful regulation. If this process is carried too far, the finished plate or film will be subject to fogging. After the first ripening, no more crystal growth takes place.

3. *Washing.*—At the close of the first ripening process, the balance of the gelatine, previously soaked in water, is added slowly with thorough stirring. The emulsion is then cooled to about 10°C. to produce a firm jelly. It is important to chill the emulsion as quickly as possible, so that the ripening process is suddenly interrupted at the proper point. In order to attain maximum solidity, the emulsion may be permitted to stand overnight in refrigerated rooms, or it may be chilled in silver-plated metal pans cooled with brine. The latter method allows the next step to proceed after 2 to 3 hr.

The cold jellied emulsion is shredded into small "noodles," 2 to 5 mm. in diameter. This is accomplished in the noodle press, where a piston operating in a silver-plated cylinder of bronze or nickel, forces the jelly through a screen (see Fig. 1). The noodles are dumped into a wire basket set in a wooden or stoneware tank, where they are washed for several hours in cold running water (less than 10°C.) to remove free NH_3, KNO_3, NH_4NO_3, and excess KBr. A careful control of the washing process is essential, as a certain amount of residual KBr is highly desirable in the emulsion to inhibit fogging during development. Some hardness in the wash water is desirable, as bivalent cations inhibit swelling of the gelatine.[1] Consequently a solution of $CaSO_4$ is used frequently for the wash water.

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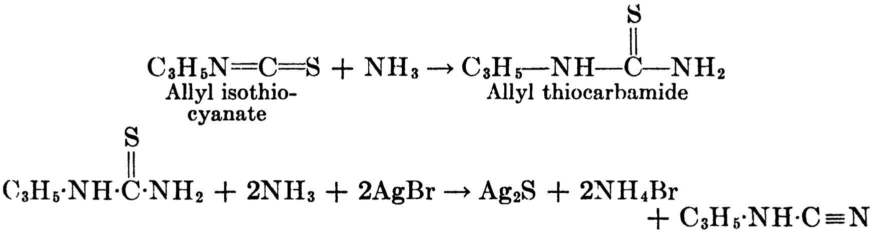
[1] Hanson, The Preparation of Photographic Emulsions, *Am. Phot.*, **35**, 560–566 (1941).

4. *Afterripening.*—The emulsion noodles are freed as much as possible from mechanically adhering water by drainage. They are next melted at about 45°C. Gelatine may be added to compensate for the water carried by the swollen noodles. The noodles are digested for some time at 50°C. in the afterripening or second ripening tank as depicted in Fig. 1. No crystal growth takes place during this treatment, the chief effect of which is an increased sensitivity due to the formation of minute activated centers of Ag_2S by a reaction of the halide with sulfur-containing substances occurring in the gelatine.[2] These are allyl isothiocyanate (mustard oil) and related compounds. In the case of the ammonia process the afterripening may be omitted, since most of the Ag_2S centers are probably formed during the first ripening, presumably by the following reactions:[1]



$$\underset{\text{Allyl isothio-cyanate}}{C_3H_5N{=}C{=}S} + NH_3 \rightarrow \underset{\text{Allyl thiocarbamide}}{C_3H_5{-}NH{-}\overset{\overset{S}{\|}}{C}{-}NH_2}$$

$$C_3H_5{\cdot}NH{\cdot}\overset{\overset{S}{\|}}{C}{\cdot}NH_2 + 2NH_3 + 2AgBr \rightarrow Ag_2S + 2NH_4Br + C_3H_5{\cdot}NH{\cdot}C{\equiv}N$$

If the afterripening process is carried too far, a decrease in sensitivity begins to occur. Emulsions containing iodide can be ripened for a longer time without fog formation than can pure bromide emulsions. For this reason a much higher sensitivity can be obtained with the former type.

Before coating the emulsion on the support, it is customary to add chrome alum or formaldehyde as a hardening agent. Phenol or thymol may be introduced to prevent the growth of mold or bacterial attack. The addition of KBr at this stage is an aid in the prevention of fog. The introduction of amyl alcohol or saponin serves to depress the surface tension of the liquid emulsion, facilitating uniform foam-free spreading on the support. The sensitizing dyes for orthochromatic or panchromatic films are here added to the emulsion. The molten emulsion is filtered and is then ready to be coated on the support.

Preparation of the Support.—The support for the photographic emulsion can be of glass, paper, nitro-cellulose, or cellulose acetate. Before 1888 glass was universally used. In that year George Eastman designed his first roll-film camera. Glass plates are still essential for many scientific and commercial purposes, map making, and some copying and color printing jobs. Glass has the advantages of freedom from distortion and not deteriorating with age. Glass plates are made from high-quality, thin sheet glass. Their preparation for the emulsion includes preliminary inspection and automatic cleaning by revolving brushes in a strong soda solution. They are coated with a thin substratum of gelatine containing chrome alum, dried in ovens, inspected, packed in trays, and transferred to the coating room.

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[1] CARROLL, *op. cit.*

[2] HANSON, *op. cit.*

FIG. 2.—Photographic film coating machine.

Nitrate film is made by running a filtered and deaerated solution of cellulose nitrate in alcohol-ether, onto a heated, rotating drum as shown in Fig. 2. The latter is made of iron, coated with nickel or silver. A typical solvent formula is 18 gal. ethyl alcohol, 36 gal. ethyl ether, 0.6 gal amyl alcohol, and 10 lb. of camphor per 100 lb. of dry nitro-cellulose. By the time the drum has made one revolution, the solvent has evaporated and the film is stripped off, wound into rolls, and transferred to the coating rooms. The solvent may be recovered by adsorption on activated carbon.

The cellulose acetate for "safety film" has an acetyl content of 39.5 to 42.0 per cent. It is insoluble in chloroform but dissolves in acetone Chloroform-soluble acetate is not strong enough for photographic film. To decrease the tendency of cellulose acetate to stretch in water and shrink after drying, substances such as triphenyl phosphate are generally added.

Both nitrate and acetate films are given a thin undercoat or substratum (the "subbing") of gelatine and chrome alum to increase the adhesiveness of the light-sensitive emulsion. The base for photographic papers is coated with gelatine containing blanc fixe (precipitated barium sulfate) to mask the cellulose impurities from the halide salts. Sometimes china clay or satin white (a coprecipitate of calcium sulfate and aluminum hydroxide) is used instead of blanc fixe.

Coating.—Glass plates are coated on a traveling belt, the fluid emulsion flowing onto the glass surface. The coated glass then proceeds onto a belt or rollers which are kept wet with ice-cold water to set the emulsion. The plates are removed, dried, cut into requisite sizes, and packed.

In coating both films and papers, the base moves on rollers into the coating trough containing the liquid emulsion as represented in Figs. 1 and 2. The excess emulsion draining off as the support leaves the trough produces a uniform coat. The coated base passes over a chill roll or into a cooling chamber to set the emulsion. After leaving the chill roll or chamber, the film or paper is automatically looped into festoons 5 to 20 ft. long, which are moved slowly through a drying tunnel supplied with warm, filtered air.

The finished film is spooled for use. Naturally the preparation of the emulsion and its coating onto the base must be conducted in air-conditioned rooms, illuminated only with lights for the particular emulsion being manufactured.

Color Photography.[1]—Natural-color processes can be divided into two classes: additive and subtractive processes. In the former the colored light reflected or transmitted by each image is transferred directly to the observer's eye, independent of the other images; in the subtractive processes the light first passes through a number of the images in succession. Each image subtracts or removes certain of the light components, until the final transmitted total contains only those components necessary to reproduce the original colors.

The additive processes of modern importance are the mosaic-screen ones, known as Agfa color, Autochrome, Dufay color, and the Finlay process. In these processes the image plane contains tiny differential areas, each of which acts as a color filter. The sum total of light from all these areas produces, to the eye, a colored image.

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[1] Henney, "Color Photography for the Amateur," McGraw-Hill Book Company, Inc., New York, 1938; Harrison, Theory of Additive Three-color Photography, *Phot. J.*, p. 706, December, 1939; Spencer, Colour Photography in Practice, Sir Isaac Pitman & Sons, Ltd., London, 1938; Nelson, Natural Color Film, Galleon Publications, Inc., New York, 1937.

In the subtractive processes, the final positive is the composite sum of the effects produced by three (or more) transparencies superimposed one upon the other. In the reversal subtractive processes (Kodachrome and Agfa-neuchrome), the color transparency is produced directly; in the remaining processes, separation negatives are made which must be printed by one of the color printing processes, all of which are subtractive. These latter processes include (1) imbibition dye printing, Eastman Washoff Relief, Defender Chromo-relief, and Curtis Orthotone, (2) imbibition ink printing, Bromoil Transfer, (3) tricolor pigment printing, Carbro process, (4) metal toning, Chromatone process.

In addition, there are certain recently announced processes in which the reversal emulsion mentioned above is used for printing. These are Kotavacolor, which is a Kodachrome emulsion on an opaque cellulose acetate base and Kodacolor prints which are composed of Kodacolor emulsion layers on a paper base.

Although three-color separation negatives can be made in a standard film-pack camera by means of a specially constructed so-called *tripack*, it is much more satisfactory to employ a special single-mirror or double-mirror camera, in which three or more selectively sensitized films are exposed singly, but simultaneously, to record each its special color, the composite of which is the true color reproduction.

Photomechanical Reproduction.[1]—Photography finds one of its most important modern applications in the reproduction of photographs on the printed page by means of printing inks. These processes may be classified as (1) relief printing (photoengraving), (2) intaglio printing (photogravure, rotogravure, and metal engraving), and (3) planographic printing (lithography, photolithography).

In *relief* printing the raised portion of a plate receives the ink for transference to the paper. So-called *line* plates and half-tone plates are used. The line plates are prepared by exposing a negative against a zinc plate coated with sensitive albumen and ammonium dichromate. The exposed zinc positive plate is coated with greasy ink and washed with warm water to remove the unexposed light-sensitive coating. Topping powder (dragon's blood) is next dusted on the remaining inked areas and burned in to form an acid-resistant layer, after which the plate is immersed in nitric acid to dissolve out the exposed areas, leaving the image in relief upon the plate, to which the ink adheres in printing.

Half-tone plates are made by copying the picture on standard photographic film through a half-tone screen, which produces a dot pattern of different intensity and then engraving in the manner described above, using, instead of zinc, a copper plate. The half-tone screen is made by ruling a series of fine straight lines on a plate of high-grade optical glass and filling the grooves with opaque pigment. The lines are ruled at an angle of 45 deg. with the vertical. Two such plates, with their lines crossing at right angles, are cemented together to produce the "screen." Fidelity of reproduction is controlled by the fineness of the screen used, the coarsest being 55 lines per inch and the finest 400 lines per inch.

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[1] GROESBECK, "The Process and Practice of Photoengraving," Doubleday, Doran & Company, Inc., New York, 1924; HACKLEMAN, "Commercial Engraving and Printing," Commercial Engraving Publishing Co., Indianapolis, 1924; MERTLE, *et al.*, "Photolithography and Offset Printing," Graphic Arts Publishing Co., Chicago, 1937.

With *intaglio* printing, the procedure is reversed from relief printing, the hollow regions of the plate holding the ink. In photogravure intaglio printing, a positive transparency is made and brought in contact with a sheet of dichromated gelatine and exposed to light, insolubilizing the gelatine in the light areas of the photograph. Meanwhile, a copper plate has been coated with finely powdered resin, which is burned onto the plate. The gelatine sheet is softened in water and placed in contact with the copper plate. It is immersed in water to remove the backing and finally further washed in warm water to dissolve the gelatine that composed the dark portions of the original picture. The plate is now etched with iron perchloride, the insoluble gelatine retarding selectively the rate of etching on the various portions to which it has adhered. The resultant copper image is iron-faced by electroplating.

Rotogravure is similar to photogravure, except that a metal cylinder instead of a plate is used, and a "screen" similar to the half-tone screen is employed for the gelatine image described above.

Planographic printing, or *lithography*,[1] makes use of the inability of a water-wet surface to take ink. A zinc or aluminum plate is roughened in order to make it capable of retaining water and coated with dichromated albumen. A line negative, or half-tone negative prepared as described above, is exposed in contact with the plate, after which the insolubilized image is coated with a greasy ink and the whole soaked in warm water to remove the soluble albumen. Subsequent etching with acid gum arabic renders the exposed surface repellent to ink but does not attack the metal. A water solution of gum arabic, next added, protects the bare portions of the lithographic plate, which is printed by the so-called *offset printing* process. Lithographic plates are particularly adaptable to illustrative work in color, the usual separation negatives being used in their preparation.

Blueprinting.—This widely used reproductive process is dependent on the fact that ferric ions are reduced to ferrous ions in the presence of organic matter and under the influence of strong light. Paper is coated with a solution of ferric ammonium citrate and potassium ferricyanide.

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[1] Originally lithography meant engraving on stone and printing therefrom. The employment of stone is not favored now except for small jobs.

If a line drawing is placed over such a prepared paper, exposed to strong light, and treated with water (as both a developing and fixing agent), the blue image appears wherever the light reduced the ferric ion. The image is the insoluble blue ferrous ferricyanide, $Fe_3[Fe(CN)_6]_2$.

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CHAPTER XXIV

PAINT, VARNISH, LACQUER, AND ALLIED INDUSTRIES

The use of organic surface-protecting coatings is of the utmost importance in preserving the country's homes, churches, buildings, and factories from the ordinary attacks of the weather. Uncoated, or as we say "unpainted," wood and steel are particularly susceptible to deterioration especially in the cities where soot and sulfur dioxide accelerate such action. The "paint-up" campaign should be supported by everyone, for it protects the capital of the nation invested in structures.

TABLE 1.—PRODUCTION OF PAINTS, VARNISHES, LACQUERS, AND ALLIED PRODUCTS[a]

	1937	1939
Paints, total value	$200,846,090	$190,459,858
Water paints and calcimines (dry or paste), lb	150,876,090	138,308,902
Paints in paste form, lb	269,826,849	253,895,535
Value	$ 28,540,716	$ 25,113,592
Varnishes, lacquers, enamels, and japans, total value	$226,002,701	$216,579,605
Varnishes, value	$ 64,730,411	$ 63,608,132
Varnish stains, gal	2,160,801	2,229,952
Value	$ 3,567,419	3,577,317
Nitro-cellulose (pyroxylin) products, value	$ 72,272,824	$ 64,301,131
Enamels, total value	$ 75,270,124	$ 75,943,835
Drying japans and driers, gal	3,522,010	2,700,148
Value	$ 2,946,870	$ 2,211,302
Baking japans, gal	3,266,880	1,939,737
Value	$ 2,507,547	$ 1,541,047
Other products of the varnish group, value	$ 4,707,506	$ 5,390,841
Fillers, total value	$ 2,110,756	$ 1,831,559
Putty, lb	90,544,189	103,232,417
Value	$ 3,683,418	$ 3,811,368
Bleached shellac, lb	14,639,005	16,282,716
Value	$ 2,664,351	$ 3,165,340

[a] *Chem. and Met. Eng.*, **48**, No. 2, 115 (1941).

Apart from their purely protective action, paints, varnishes, and lacquers, by their decorative effect, greatly increase the attractiveness and aesthetic appeal of a community of homes or the interior of a room. Here is a case where art and utility proceed hand in hand. Indeed some of the research toward obtaining longer lasting out-of-door paint has enabled the manufacturers of artists' colors to produce more permanent colors for purely artistic purposes.

Historical.—The surface-coating industry is indeed an ancient one. The origin of paints dates back to prehistoric times when the inhabitants of the earth recorded some of their activities in colors on the walls of their caves. These crude paints consisted probably of colored earths or clays suspended in water. The Egyptians, starting very early, developed the art of painting and by 1500 B.C. had a wide number and variety of colors. Around 1000 B.C. they discovered the forerunner of our present-day varnishes, using naturally occuring resins or beeswax for their film-forming ingredient. Pliny outlined the manufacture of white lead from lead and vinegar, and it is probable that this ancient procedure resembles the old Dutch process. It is in more recent years, however, that the surface-coating industry has made its greatest strides owing to the results of scientific research.

Uses and Economics.—The manufacture of paints, pigments, lacquers, and varnishes is an industry which has an annual production value of well over $500,000,000 and whose products are of vital importance in our everyday life. Table 1 gives a comprehensive economic picture of the industry as a whole.

PAINTS[1]

Paints have been defined[2] as "colored mixtures, usually liquids, with which suitable surfaces can be coated by a brush or other means; the covering formed may be dull or lustrous and acts as a *protective* and *preservative* of the surface beneath it."

Constituents.—The constituents of paints are outlined in Table 2. The *pigment*, while usually an inorganic substance, may also be a pure insoluble organic dye known as a *toner* or an organic dye precipitated on an inorganic carrier such as aluminum hydroxide, barium sulfate, or clay, thus constituting a *lake*. Pigment *extenders* or *fillers* act to reduce the cost of the paint and frequently to increase the durability. The function of the pigments and the fillers is not to provide simply a colored surface pleasing for its aesthetic appeal, important as that may be. The solid particles in the paint reflect away much of the destructive light rays and thus help to prolong the life of the entire paint. In general, pigments should be *opaque* to ensure good covering power and be *chemically inert* to secure stability and hence long life. The pigments now acceptable should be *nontoxic* or at least of very low toxicity to both the painter and the inhabitants. Finally the pigments must have *mixing ability* toward the film forming oils and be of *low cost.* Different pigments possess different covering power per pound. Table 3 evaluates some white pigments in terms of cost per 100 sq. ft. painted; however, weathering ability is not considered.

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[1] A series of four volumes is appearing under the editorship of Joseph Mattiello, entitled "Protective and Decorative Coatings, Paints, Varnishes, Lacquers, and Inks." These are published by John Wiley & Sons in New York, the first volume in 1941. These should be consulted by anyone wanting detailed knowledge of any phase of this field.

[2] THORPE, "Dictionary of Applied Chemistry," 3d ed., Longmans, Green and Company, New York, 1928.

Without *film-forming materials,* the pigments would not be held onto the surface. These paint films are formed by the "drying" of various unsaturated oils such as are listed in Table 2 and further described in Chap. XXVIII. The drying is a chemical change representing polymerization and oxidation; it is hastened by pretreatment of the oil, as in boiling the linseed oil, and by adding the *driers* which are oxygen carriers usually soluble in oil. These driers need be employed in only small amounts of the order of 1 part of metal to 1,000 parts of the paint.

As paints are mechanical mixtures, the pigments and extenders are carried or suspended in a *vehicle.* This vehicle is the film-forming oil to which other liquids are added in varying amounts not only in the factory but by the painter on the job. The *diluent* or *thinner* used for this purpose is a volatile liquid like turpentine or turpentine substitute, the latter usually being a petroleum naphtha of the approximate evaporating rate of turpentine. To reduce certain aspects of cracking or livering in paints, *plasticizers* are being introduced into the formulas, largely by proper choice of the oils.

Manufacturing Procedures.—The various operations needed to mix paints are wholly physical. These *unit operations* are shown in proper sequence in the flow sheet[1] of Fig. 1. Chemical changes or *unit processes* are involved in the manufacture of the constitutents of paints as well as in the drying of the film.

A modern paint factory may consume 2,000 raw materials and produce ten times that number of finished products, so great is the variety of surface coatings needed for public demands. The manufacturing procedures illustrated in Fig. 1 and described here are for a mass-production paint. The first operations are housed on the top floor so that, as manufacturing continues, the materials can be transferred easily and economically from floor to floor by gravity. The weighing, assembling, and mixing of the

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[1] A pictured flow sheet is given in *Chem. & Met. Eng.*, **46**, 157 (1939).

TABLE 2.—PAINT CONSTITUENTS

Class	Ingredient	Function
1. Film-forming materials	*Drying oil:* Linseed oil Tung oil Perilla oil Fish oil Soybean oil Oiticica oil Castor oil, dehydrated	To form the protective film through oxidation and polymerization of the unsaturated constituents of the drying oil
2 Pigments	*White* White lead Zinc oxide Lithopone Titanium dioxide Blanc fixe Basic lead sulfate *Black* Carbon black Lampblack Graphite *Blue* Ultramarine Cobalt blues Copper phthalocyanine Iron blues *Red* Red lead Iron oxides Toners and lakes *Yellow:* Litharge Ocher Lead chromate *Green:* Chromium oxide Chrome green *Brown:* Burnt sienna Burnt umber Vandyke brown	To protect the film by reflecting away the destructive ultraviolet light, to strengthen the film, and to impart an aesthetic appeal. Pigments should possess the following properties. opacity and good covering power, mixing ability with oil, chemical inertness, non- or low toxicity, reasonable cost

TABLE 2 —PAINT CONSTITUENTS —(*Continued*)

Class	Ingredient	Function
	Metallics: Aluminum Zinc dust	
3 Pigment extenders or fillers	China clay Talc Asbestos (short fibers) Silica Whiting Gypsum	To reduce the pigment cost, and, in many cases, to increase the covering and weathering power of pigments by supplementing pigment particle size
4 Vehicles	Turpentine Any other liquids (*cf* 1 and 6)	To suspend pigments and to dissolve film-forming materials, thus enabling paints to be applied
5 Driers	Pb, Mn, Co resinates, linoleates, oleates, acetates, or oxides	To hasten the drying or hardening of the film by carrying oxygen
6 Diluents	Turpentine "Turpentine substitute" (petroleum)	To thin concentrated paints for better handling by brushing or spraying
7 Plasticizers	Some oils	To give elasticity to film, thus preventing or minimizing cracking or livering

pigments and vehicles are done on the top floor. The mixer may be similar to a large dough kneader

The batch masses are conveyed to the floor below, where grinding and further mixing take place A variety of grinding mills may be used.

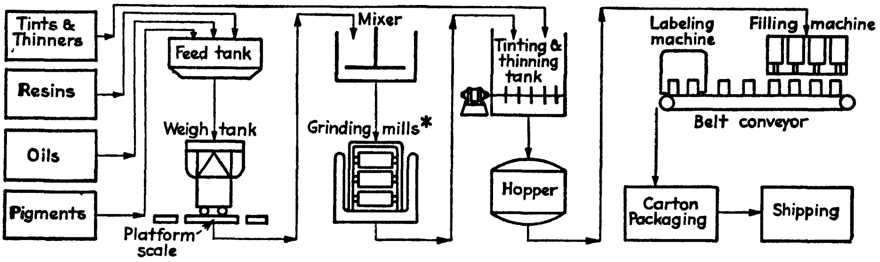
TABLE 3 —RATIO OF COSTS OF WHITE PIGMENTS PER 100 SQ FT OF SURFACE PAINTED[a]

Pigment	Ratio
Lithopone	1
Titanox	1.08
Zinc oxide (American)	1.34
White lead	1.93
Basic lead sulfate	2.47

[a] Titanium U S Bur *Mines Circ* 34 1933

One of the oldest methods is grinding between two buhrstones; in modern mills these are driven by electricity. Steel roller mills using as many as five rolls or pebble mills are generally used now. It is very important to have correct proportions of pigments and vehicles in grinding. Table 4 gives some typical proportions for certain pigments.

This mixing and grinding of pigments in oil require much skill and experience to secure a smooth product without too high a cost. Perry[1] presents these unit operations in a very useful manner with pictures of various mills and tabulations of the engineering factors concerned.



NOTE: Because a complete paint factory consumes upward of 2,000 different raw materials and produces ten times as many finished products, it is not possible to gives yields, etc.

** Many types of grinding mills are used in the same plant either in series or in parallel. Some of them are: buhrstone, coffee, and single-, three- and five-roll steel mills*

FIG. 1.—Flow sheet for mixing of paint.

TABLE 4.—CORRECT GRINDING PROPORTIONS FOR SEMIPASTE COLORS IN LINSEED OIL[a]

Colors	Pigments, per cent	Oil, per cent	Bulking value, semipaste, gal. per 100 lb.
Basic lead carbonate	80	20	4.0
Lithopone	70	30	5.82
Carbon black	20	80	11.65
Ultramarine blue	45	55	9.40
Chrome yellow	70	30	5.29
Graphite	35	65	10.18

[a] PERRY, *op. cit.*, p. 1981.

The paint is transferred to the next lower floor, where it is thinned and tinted in large 600-gal. tanks, each equipped with an agitator. The liquid paint is screened into the hopper of the filling machine on the floor below. The paint is filled into cans, labeled, packed, and moved to storage, each step being completely automatic.[1]

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[1] *Op. cit.* See following pages for the items noted: pp. 1532–1533 for physical factors in mixing with explanation of viscosity and its opposite, fluidity—as well as of plasticity and its opposite, mobility; pp. 1536–1539 for apparent viscosity or consistency with consistency curves for classification of paints; p. 1568 for mixing liquids and solids with various consistencies as measured in centipoises; p. 1547 for pony mixer; p. 1546 for mixers with stationery fingers; p. 1549 for kneaders; pp. 1892 (*i*) and 1978 for roller mill; pp. 1893 (*p*) and 1980 for buhrstone mill; p. 1979 for power required and operating characteristics of roller mills; pp. 1892 (*d*) and 1980 (*l*) for pebble mills.

Paint Failure.—The failure of paints to stand up under wear may be due to several causes, and in each case there is a special term used to describe the failure. *Chalking* is a progressive powdering of the paint film from the surface inward and is caused by continued and destructive oxidation of the oil after the original drying of the paint. *Peeling* is due to poor attachment of the paint to the surface being covered and is usually attributed to dirt or grease on the surface or to water entering from behind the paint. *Flaking* is caused by small sections of paint leaving the surface for the same reason that causes peeling. *Alligatoring* is a form of peeling in which the center portion of the section starting to peel remains attached to the surface. As opposed to these methods of paint failure, normal wear is the gradual removal of paint from the surface by the elements, leaving a smooth surface behind.

Paint Application.—Much application of paint is still done by hand brushes, but dipping or spray painting is gaining favor with some because of the ease and rapidity of spread, thus saving labor though it may waste a little material. A wide variety of types of atomizers for spraying is available, including internal mixing and the more common external mixing. Spray guns are operated frequently at a pressure of 40 to 60 lb. per sq. in. Four to 8 cu. ft. of free air per minute are required at 40 lb. per sq. in.[2] A surface that is efficiently painted, varnished, or lacquered generally requires the application of a number of different coats of composition varied to suit the condition. For example, most surfaces require the use of a primer or filler coat to smooth over inequalities and to secure better adherence. This may then be covered with the paint proper in several applications.

PIGMENTS

Pigments[3] are used very widely in surface coatings but are also employed in the ink, plastic, rubber, ceramic, and linoleum industries.

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[1] For a somewhat more detailed account of paint manufacture as well as numerous pictures of equipment, see Anon., Modern Equipment—Better Paint, *Chem. & Met. Eng.* **46**, 157 (1939). For a description of modern paint equipment see also *Paint, Oil, Chem. Rev.*, **103**, No. 5, 8–9 (1941). For a very excellent short (47 pp.) presentation of Organic Protective Coatings, see Chap. 19 under this title in Leighou, edited by Warner, "Chemistry of Engineering Materials," 4th ed., McGraw-Hill Book Company, Inc., New York, 1942.

[2] PERRY, *op. cit.*, pp. 1989, 1994–1996.

[3] Mattiello, *op. cit.*, vol. 2, 1942, gives a very full account of pigments in all phases, with full references to the literature. See this reference for further data on any individual pigment. In the use of pigments, a very important aspect is consistency. For this *cf.* Dunn, Kushner, and Baier, Effect of Particle Size and Shape on Paint Consistency, *Ind. Eng. Chem.*, **33**, 1157 (1941). References to other articles are included.

A large number of pigments and dyes are consumed because different products require a particular choice of material to give maximum coverage, economy, opacity, color, and durability. Twenty years ago white lead, zinc oxide, and lithopone were the principal white pigments; colored pigments consisted of Prussian blue, lead chromates, various iron oxides, and a few lake colors. Today we find among the new pigments titanium oxide in many varieties, chromium oxides and hydrates, and a host of organic colors. Table 5 exhibits recent figures on the production of pigments.

WHITE PIGMENTS

White Lead.—The oldest and one of the most important of the white pigments is white lead,[1] which has the approximate formula $2PbCO_3\cdot Pb(OH)_2$.

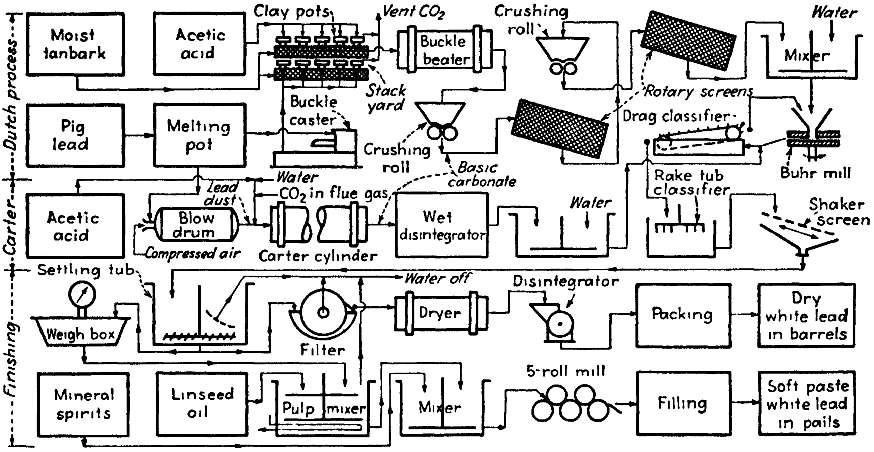

FIG. 2.—Flow charts for white lead—Dutch and Carter processes.

Paints made from white lead are very easily applied and have a high covering power. They have the disadvantages of reacting with sulfur-containing gases and of becoming chalky and wearing off. These disadvantages have been largely overcome by mixing white lead with other pigments as zinc oxide as well as with pigment extenders such as barium sulfate and barytes.

In the *Dutch process*[2] of manufacture (Fig. 2), lead is melted and cast in the form of 6-in. perforated disks or "buckles," which are placed on a shelf in small earthenware pots containing 3 per cent acetic acid (vinegar strength) in reservoirs underneath and not in contact with the lead buckles. The pots are then stacked in tiers, covered with boards, and arranged 10 tiers high. Spent tanbark is placed all around the pots, and the rooms are closed off. During a period of about 100 days, the acetic acid vapors, moisture, and the carbon dioxide gas from the warm fermenting tanbark act on the lead to give the flaky white lead or basic lead carbonate. This is broken away from any unreacted lead, ground, floated in water, and dried to give the product which contains about 70 per cent carbonate and 30 per cent hydroxide.

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[1] MATTIELLO, *op. cit.*, vol. 2, p. 337.

[2] Pictured flow chart, *Chem. & Met. Eng.*, **50**, No. 3, 130 (1943).

TABLE 5.—PRODUCTION OF PIGMENTS[a]

	1937	1939
White lead (basic carbonate) and sulfate, lb	144,313,029	119,571,570
Value	$ 9,450,759	$ 7,115,870
Lead oxides, total value	$ 18,854,145	$ 15,918,767
Litharge		
Made and consumed, lb	44,216,684	32,340,072
Made for sale and interplant transfer, lb	165,628,019	164,454,772
Value	$ 12,102,184	$ 9,230,853
Red lead, minium, lb	90,223,322	104,881,475
Value	$ 6,751,961	$ 6,687,914
Zinc oxide, lb	321,889,816	301,895,235
Value	$ 15,316,173	$ 14,431,992
Lithopone, total production, lb	366,018,427	313,568,246
Made and consumed, lb	40,918,543	30,364,024
Made for sale and interplant transfer, lb	325,099,884	283,204,222
Value	$ 13,760,312	$ 11,973,519
Iron oxides (natural and synthetic), lb	128,891,324	101,949,630
Value	$ 4,067,840	$ 3,275,941
Titanium dioxide, lb	No data	161,708,130
Value	No data	$ 17,422,336
Other oxides, lb	328,138,379	203,614,895
Value	$ 22,458,369	$ 8,942,792
Other mineral colors, lb	152,105,207	31,207,511
Value	$ 6,688,338	$ 1,644,802
Other fine color pigments, lb	12,397,763	16,285,783
Value	$ 2,689,443	$ 4,096,431
Whiting, total production, lb	147,313,121	131,411,553
Made and consumed, lb	23,318,491	21,695,120
Made for sale and interplant transfer, lb	123,994,630	110,716,433
Value	$ 866,736	$ 764,941

[a] *Chem. & Met. Eng.*, **43**, No. 2, 115 (1941). Although more recent figures are not available in the detail given in this table, it may be stated that practically all of the above pigments are being produced in considerably increased amounts.

In the *Carter*[1] *or "quick" process* (Fig. 2), the melted lead is atomized by spraying from nozzles by means of air or superheated steam. This finely divided lead is periodically treated or "corroded" with a spray of

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[1] FERGUSON, White Lead, U.S. Pat., 2250756 of 1941; *Chem. & Met. Eng.*, **50**, No. 3, 130 (1943), pictured flow chart.

acetic acid, purified carbon dioxide gas from coke, and air in a large slowly revolving wooden cylinder to give the white lead after some 5 to 12 days. This material is whiter, finer, and more uniform than the old Dutch lead.

The reactions for the old Dutch and the Carter processes are as follows:

$$\mathrm{Pb} + \tfrac{1}{2}\,\mathrm{O_2} \rightarrow \mathrm{PbO}$$

$$\mathrm{PbO} + 2\mathrm{CH_3COOH} \rightarrow \mathrm{Pb(C_2H_3O_2)_2} + \mathrm{H_2O}$$

$$\mathrm{Pb(C_2H_3O_2)_2} + 2\mathrm{PbO} + 2\mathrm{H_2O} \rightarrow \mathrm{Pb(C_2H_3O_2)_2{\cdot}2Pb(OH)_2}$$

$$3[\mathrm{Pb(C_2H_3O_2)_2{\cdot}2Pb(OH)_2}] + 4\mathrm{CO_2} \rightarrow 2[\mathrm{2PbCO_3{\cdot}Pb(OH)_2}] + 3\mathrm{Pb(C_2H_3O_2)_2} + 4\mathrm{H_2O}$$

A third method of manufacture is the *electrolytic process* wherein the reaction is carried out by means of a concrete electrolytic diaphragm cell made up of lead plates as anodes, suspended in a sodium acetate solution (containing a trace of sodium carbonate), and iron plates as cathodes, suspended in a sodium carbonate solution. The two divisions of the cell are separated by a fabric diaphragm. Upon the application of current, the lead anodes dissolve as lead acetate which almost immediately precipitates as the basic lead carbonate upon meeting carbonate and hydroxide ions migrating toward the anode from the cathode compartment. The white lead is carried out of the cell with the anolyte and is settled, filtered, washed, and dried to give the final product. As the carbonate ions in the catholyte diffuse through the diaphragm and are precipitated, circulation of the catholyte through a carbonating tower is necessary.

Sublimed White Lead (Basic Sulfate).—A pigment closely related to ordinary white lead is sublimed white lead or *basic sulfate* as it is sometimes called. It is made by the sublimation of galena ores which are essentially lead sulfide, PbS, together with a small amount of zinc sulfide. The product, mainly basic lead sulfate with a small percentage of zinc oxide, is much more resistant to the action of sulfur than ordinary white lead. The composition is approximately 75 per cent $\mathrm{PbSO_4}$, 20 per cent PbO, and 5 per cent ZnO. Note that it is made directly from the ore and is consequently priced reasonably.

Zinc Oxide.—Another important white pigment is zinc oxide,[1] ZnO, which has been in use for over a century. Zinc oxide as a pigment does not have the opacity or covering power of white lead; on the other hand it is the truest white that can be obtained and its color is unaffected by gases in the atmosphere. Zinc oxide prevents premature chalking through the formation of zinc soaps and through its high opacity toward ultraviolet rays. Zinc oxide also reacts with the linseed oil to harden the film.[1] The methods employed to produce this pigment are the American or Wetherill process, the older French process, and the electrothermal process. The three processes may be broken down into the following sequences of *unit operations* (Op.) and *unit processes* (Pr.):

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[1] Mattiello, *op. cit.*, vol. 2, p. 369; Nelson, Zinc Oxide, *Chem. Industries*, **47,** 508 (1940). See Chap. 25 by Sward in "Rogers' Manual of Industrial Chemistry," 6th ed., D. Van Nostrand Company, Inc., New York, 1942.

American Process	*French Process*	*Electrothermal Process*
Reducing of ZnO by CO and C (Pr.)	Vaporization of zinc (Op.)	Roasting to ZnO (Pr.)
Vaporization of zinc (Op.)	Oxidation to ZnO (Pr.)	Sintering (Pr. and Op.)
Oxidation to ZnO (Pr.)	Separating and collecting (Op.)	Sizing (Op.)
Settling, separating, and collecting (Op.)	Revolatilization of coarse oxide (Op.)	Preheating and electrothermal volatilizing of Zn (Pr. and Op.)
Bolting, packing (Op.)	Bolting, packing (Op.)	Oxidizing to ZnO (Pr.)
		Separating and collecting (Op.)
		Bolting, packing (Op.)

ZnO + Co + C → Zn-vap.

The *American* or *Wetherill* process, used where whiteness is not an important factor, produces the zinc oxide directly from the ore, franklinite, which is a zinc oxide with oxides of iron and manganese. This ore is mixed with coal and delivered to a specially designed furnace. Here carbon and carbon monoxide reduce the zinc oxide of the ore to metallic zinc which is vaporized and reoxidized to ZnO upon contact with the air from the furnace, as shown in Fig. 3. The product is collected, the coarse in cyclones and the fines in bag filters. The larger particles are returned to the process. The residue from the furnace contains manganese and iron from the original franklinite, as well as carbon from the coal, and is sometimes used to make spiegeleisen, a manganese alloy. Through the addition of galena, PbS, during the process, a content of lead sulfate can be secured, producing the so-called *leaded* zinc oxides, containing up to 35 per cent lead sulfate. This product would have the analysis[2]: ZnO, 65 per cent; PbO, 9 per cent; $PbSO_4$, 26 per cent.

The *French process*, as may be seen from the accompanying flow sheet (Fig. 3), consists in vaporizing zinc (spelter) in a retort with indirect heat and carbon monoxide gas, and then oxidizing both the zinc vapor and the carbon monoxide by meeting a current of preheated air in a combustion chamber. The reducing gas, CO, aids in the volatilization of the zinc. When it burns, it forms carbon dioxide simultaneously with the change of zinc vapor to zinc oxide. Under these conditions the lead that frequently accompanies the zinc forms white lead. Otherwise yellow PbO would be produced and cause the zinc oxide to possess a yellowish tinge. The larger particles of the oxide are removed in a settling chamber, while the fines are collected in bag filters. After revolatilizing the coarse oxide in the reheat furnace, both products are ready for bolting, packaging, and shipping.

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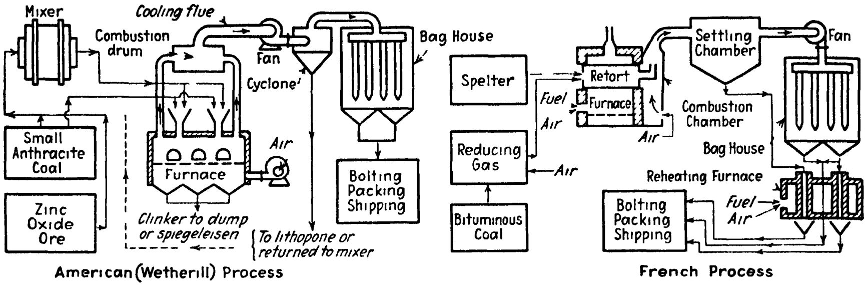
[1] JOACHIM, "Applied Paint and Varnish Chemistry," vol. I, American Paint Journal Co., St. Louis, Mo., 1934.

[2] EIDE and DEPEW, Leaded Zinc Oxide, *Drugs, Oils & Paints*, **54**, 119 (1939).



American (Wetherill) Process		To produce 1 ton ZnO (total, all grades)	French Process	
Franklinite Ore (16% Zn)	5.25 tons		Spelter	1740 lb
Coal	3.5 tons		Coal	1,390 lb
Electricity	360 kw hr		Electricity	35 kw hr
Direct labor	8 man hr		Direct labor	5 man hr

FIG. 3.—Flow sheets for zinc oxide by the American (Wetherill) and French processes

The *electrothermal process*[1] uses sphalerite, a zinc sulfide ore, and produces sulfuric acid as a by-product (Fig. 4). The concentrated ore is first roasted and the sulfur content reduced from 32 to about 1 per cent, sulfur dioxide gas produced being sent to the acid plant. The product from the roaster is ~~mixed with coke~~, fluxes, ~~and various residues~~ from previous runs and is then fed to a sintering machine. Here the material reaches temperatures ~~as~~ high as 1600°C., following which it is crushed and screened. Carefully sized coke is mixed in and the mass sent through a gas-fired preheater into the electric resistance furnace. These furnaces are around

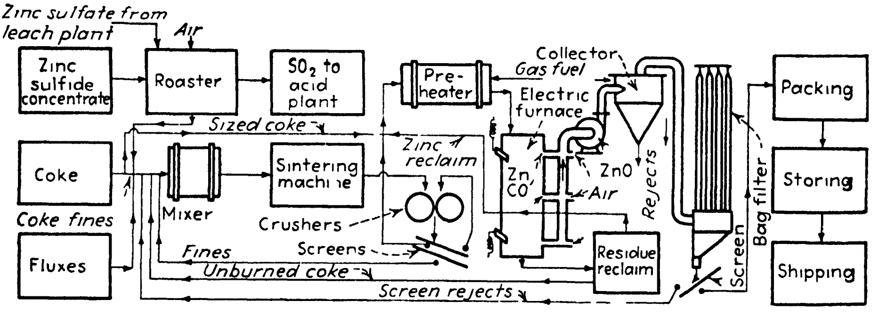


FIG. 4.—Flow sheet for zinc oxide by electrothermal process.

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[1] For a description of this process complete with pictures see *Chem. & Met. Eng.*, **48**, No. 2, 142–145 (1941).

36 ft. high and 57 in. in internal diameter and hold 55 tons. Electrodes are at the top and bottom, the charge acting as the resistance and the temperature rising to 1200°C. The gases leaving the furnaces are zinc vapor and carbon monoxide which are oxidized by the air entering at several points up the side of the furnace exit. The product is collected, screened, packed, and shipped.

Lithopone.—Lithopone, as originally prepared in 1874, had an incorrect particle size and possessed a tendency to turn temporarily gray on exposure to sunlight. However, it was discovered in 1880 that heating the product to a red heat and plunging it into water remedied the physical defect. The graying is probably caused by traces of *metallic zinc* arising from photochemical action of the sun's ultraviolet light. The whiteness is restored at night. This original light sensitiveness has been overcome by raw material purification and by such addition agents as polythionates. Lithopone now has become the most widely sold of the white pigments. It has many advantages: it is brilliantly white, it is extremely fine, it has more hiding power than zinc oxide, and it is cheap. It is particularly well adapted to interior coatings.

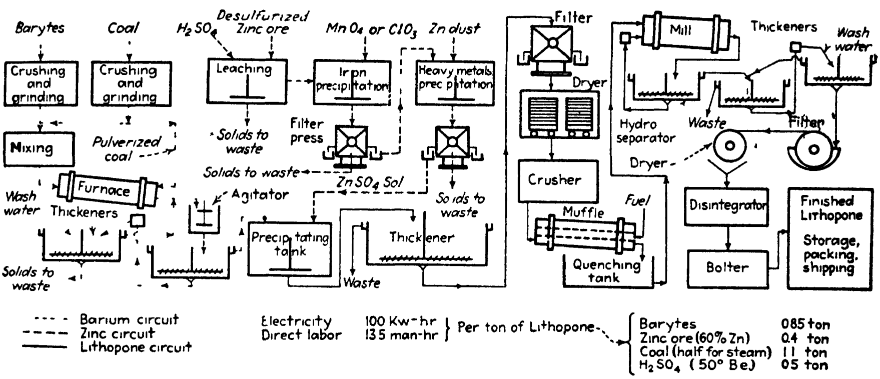

FIG. 5.—Flow sheet for lithopone.

The manufacture is shown diagrammatically in Fig. 5, where the barium, zinc, and lithopone circuits are represented by different types of lines. The barium sulfide solution is prepared by reducing baryte ore, $BaSO_4$, with carbon and leaching the resulting mass. The equation is

$$BaSO_4 + 4C \rightarrow BaS + 4CO$$

Scrap zinc or concentrated zinc ores are dissolved in sulfuric acid and the solution purified as shown in Fig. 5. The two solutions are reacted and a heavy mixed precipitate results which is 28 to 30 per cent zinc sulfide and 72 to 70 per cent barium sulfate.

$$ZnSO_4 + BaS \rightarrow ZnS + BaSO_4$$

This precipitate is not suitable for a pigment until it is filtered, dried, crushed, heated to a high temperature, and quenched in cold water. This second heating in a muffle furnace at 725°C. produces crystals of the right optical size. Subsequent treatments, as indicated, give the finished product.

Some of the variations of the original lithopone are calcium lithopone in which calcium sulfide replaces the barium sulfide in the precipitation; high-strength lithopone which contains from 50 to 60 per cent zinc sulfide due to the addition of zinc chloride to the sulfate solution; and titanated lithopone which has about 15 per cent titanium dioxide added.

Titanium Dioxide.—The most recently introduced of the important white pigments is titanium dioxide,[1] TiO_2, which is relatively costly and is usually marketed pure or as a mixture of about 30 per cent titanium dioxide on about 70 per cent barium sulfate or calcium sulfate. Ordinary titanium dioxide does not compare with other white pigments in use for exterior paints, as it chalks very badly, even when used in mixtures of other pigments. However, it has a very low cost per unit of hiding power and, in addition, makes a very excellent pigment for use in enamels and lacquers. The excellent hiding power of titanium dioxide is due to its high index of refraction (2.55) with relation to that of the film-forming oil. Other important uses of titanium dioxide are as a rubber pigment, in delustering rayon, in white plastic products, in light-colored inks, and in making white oilcloths and linoleums. However, recently it has been found possible to secure the titanium dioxide in the form of the more permanent rutile oxide which chalks less, so that its use in exterior paints is increasing. This is done by calcining the $Ti(OH)_2$ to TiO_2 in the presence of antimony oxide, for example.

The raw material for the manufacture of titanium dioxide is ilmenite, $FeO{\cdot}TiO_2$, an ore containing iron in addition to the titanium. This ore occurs chiefly in Norway and on the Indian peninsula, though there are workable deposits in Virginia, Arkansas, Australia, and other places. The ground ilmenite ore is digested in large conical tanks with 66°Bé. sulfuric acid and the mixture agitated with air and heated to 100°F. At this temperature, reaction occurs between the ore and the acid, converting the titanium to a soluble sulfate. The sequences of these unit operations and unit processes are diagrammatically presented in the flow sheet of Fig. 6. The reaction mass is then dissolved in water, giving a solution of titanium sulfate, ferrous sulfate, and ferric sulfate. The ferric sulfate is reduced to ferrous by means of scrap iron and the solution clarified in thickeners. Cooling, crystallization, centrifuging, and filtration remove some iron from the solution as crystallized ferrous sulfate. The mother liquor is heated with steam until 95 per cent of the titanium present is hydrolyzed, and the resulting titanium hydrate pulp is filtered off. This series of filtrations, washing, and further reductions serves to remove the last traces of iron. The titanium hydrate is calcined in an oil-fired kiln at about 900°C. to give the desired titanium dioxide, raising the index of refraction of the amorphous hydrate of 1.8 to 2.55 for the crystalline oxide. The final treatment consists in dispersion in water, wet grinding, thickening, filtering, drying, and air separating, all as depicted in Fig. 6. In case it is desired to make a pigment containing an extender like barium sulfate (Titanox B) or calcium sulfate (Titanox C), the exact amount of a solution of either barium or calcium chloride is added to the hydrolyzing tank. Barium sulfate or calcium sulfate precipitates at once and, in the course of the several hours of the hot hydrolysis, the titanium hydrate precipitates onto the carrier.[1]

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[1] MATTIELLO, *op. cit.*, vol. 2, p. 389.

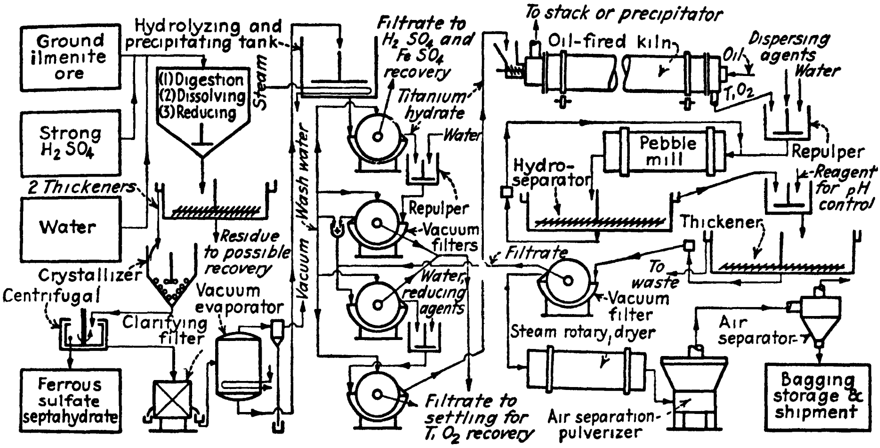

Fig. 6.—Flow sheet for titanium dioxide.

Barium Sulfate.—Barium sulfate is occasionally used as a pigment because of its great stability. It has, however, very poor covering power. On the other hand it is widely employed as a filler in rubber, or as a coating material on certain fine papers. It is opaque to X rays and consequently finds application in the form of the so-called *barium meal* for X-ray visualization of the intestinal tract.

For some of its cruder applications it is made by fine grinding and washing of the ore, barite. A better product results by precipitation, known as *blanc fixe*. Blanc fixe was produced as a by-product in the making of hydrogen peroxide, but it is now made by precipitation of a soluble barium compound, such as barium sulfide or barium chloride, by means of either sodium sulfate or sulfuric acid. Barium sulfate when intended for internal administration for X-ray diagnosis, in addition to being in the form of a very fine powder capable of giving good aqueou suspensions, must also be free from objectionable impurities such as lead, arsenic, sulfide, soluble barium salts, and the like. Since ordinary blanc fixe of commerce is not of a purity suitable for this latter use, this X-ray barium sulfate must be especially manufactured.

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[1] U.S. Pats. 1236655 and 1155462.

BLACK PIGMENTS

The chief black pigments employed are *carbon black*, *graphite*, and *lampblack*. Their manufacture is discussed under Industrial Carbon, Chap. IX. They retard the oxidation of linseed oil and cause a slow-drying film which under many conditions prolongs the life of paint. Carbon and graphite pigments should not be used in direct contact with iron and steel in primer coatings, for example, as they stimulate metal corrosion. Black dyes are also used as coloring agents; for example, spirit-soluble nigrosine finds extensive use in the formulation of black lacquers.

BLUE PIGMENTS

The most widely used blue pigment today is synthetic *ultramarine blue*. Formerly this was available only to artists as powdered *lapis lazuli*, an expensive mineral. Ultramarine is a complex sodium ~~aluminum~~ silicate and sulfide, made by heating together sodium carbonate, kaolin, charcoal, quartz, sulfur, sodium sulfate, and resin. It is absolutely essential that iron be absent in all the raw materials, as it appreciably dulls the color. The melt is cooled, ground, washed free of water-soluble salts, and heated with more sulfur at 500°C. until a blue color develops. A darker blue may be produced by substituting sodium sulfate for sodium carbonate. These pigments are stable to light and alkali but are affected by acids owing to the liberation of hydrogen sulfide. Ultramarine because of its sulfide composition should not be employed on iron or mixed with lead pigments. Ultramarine is widely used as bluing in laundering to neutralize the yellowish tone in cotton and linen fabrics. It is also applied for whitening paper and other products.

Cobalt blues are very expensive and not used in paints for ordinary purposes. One is a compound oxide of cobalt (30 to 35 per cent Co_3O_4) and alumina (70 to 65 per cent Al_2O_3); the other is a powdered glass colored by cobalt oxide. Another product, erroneously called cobalt blue, is made by the reaction of ammonium chloride on ultramarine at 200°C. The substitution of potash salts for sodium salts in the making of ultramarine gives a blue color somewhat analogous to cobalt. A newcomer in this field with a real future, particularly as a pigment in printing inks, is *copper phthalocyanine*, which is described in Chap. XXXVIII.

The various ferric ferrocyanide blues[1] are known as Prussian blue, Chinese blue, milori blue, bronze blue, Antwerp blue, and Turnbull's blue. As these names have lost much of their original differentiation, the more general term of *iron blues* is preferred. These are made in essentially the same manner by the precipitation of ferrous sulfate solutions (sometimes in the presence of ammonium sulfate) with sodium ferrocyanide giving a white ferrous ferrocyanide which is then oxidized to ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$, or to $Fe(NH_4)[Fe(CN)_6]$ by different reagents such as potassium chlorate, bleaching powder, and potassium dichromate. The pigment is washed and allowed to settle since filtration is extremely difficult because of its colloidal nature. The coloring power of Prussian blue is very great; this pigment is also permanent to light and air. It is decomposed by whiting and basic pigments such as white lead, ferric hydroxide being formed.

RED PIGMENTS

Red lead, Pb_3O_4, has a brilliant red-orange color, is quite resistant to light, and finds extensive use as a priming coat for structural steel, particularly as it possesses corrosion-inhibition properties against iron and steel. The red lead, or minium, is manufactured by oxidizing lead to litharge, PbO, in air, and further oxidizing the litharge to the red lead by heating to around 700°F.

Ferric oxide, Fe_2O_3, is another red pigment that is employed in paints and primers as well as in rubber formulation. It is made by heating the iron sulfate obtained from the pickling vats of steel mills. *Venetian red* is a mixture of ferric oxide with up to an equal amount of the pigment extender, calcium sulfate. This pigment is manufactured by heating ferrous sulfate with quicklime in a furnace. Venetian red is a very permanent and inert pigment particularly on wood. The calcium sulfate content, because of furnishing corrosion-stimulating sulfate ions, militates against the application of this pigment on iron. *Indian red* is a naturally occurring mineral whose ferric oxide content may vary from 80 to 95 per cent, the remainder being clay and silica. It is made by grinding hematite and floating off the fines for use. The basic lead chromate, $PbCrO_4 \cdot Pb(OH)_2$, may also be used as an orange-red pigment; it is also a most excellent corrosion inhibitor. It is manufactured by boiling white lead with a solution of sodium dichromate. *Cadmium reds* are made by roasting the precipitate obtained through mixing cadmium sulfate, sodium sulfite, and sodium selenide. Red pigments include a large variety of insoluble organic dyes, either in the pure state as toners or precipitated on inorganic bases as lakes.

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[1] CALLAHAM, Modernizing Chemical Color Manufacture, *Chem. & Met. Eng.*, **50**, No. 6, 106 (1943), flow charts.

YELLOW PIGMENTS

Ocher is a naturally occuring pigment consisting of clay colored with 10 to 30 per cent ferric hydroxide. It must have been ground and levigated. At best the ochers are very weak tinting colors and are being replaced by precipitated iron colors.

Yellow pigments with a wide variety of shades fall in the class known as *chrome yellows;* they are the most popular yellow pigments because of exceptional brilliance, great opacity, and excellent light fastness. They are produced by mixing a solution of lead nitrate or acetate with a solution of sodium dichromate. Extenders may be present up to an equal weight of gypsum, clay, or barite. The pigment is of high specific gravity and settles out. *Zinc chromate,* while of poor tinting power, is used because of its excellent inhibiting effect both in mixed paints and as a priming coat for steel and aluminum.

Litharge, PbO, is made by heating melted lead in a current of air. It is used to some extent in anticorrosion paints but finds a wider use as a drier.

GREEN PIGMENTS

One of the oldest green pigments is *chromium oxide,* Cr_2O_3. It has many disadvantages such as high cost and lack of brilliancy and opacity, but it is the only permanent green known. It is made by fusing a chromate or dichromate with sulfur.

$$Na_2Cr_2O_7 + S \rightarrow Cr_2O_3 + Na_2SO_4$$

It likewise results upon treating chromic sulfate with sodium hydroxide and calcining.

$$Cr_2(SO_4)_3 + 6NaOH \rightarrow 2Cr(OH)_3 + 3Na_2SO_4$$
$$2Cr(OH)_3 \rightarrow Cr_2O_3 + 3H_2O$$

Chrome green, sold under various names, is a mixture or a coprecipitation of chrome yellow with Prussian blue. Inert fillers are used with this pigment in making paints. Unless carefully ground or coprecipitated, the two colors may separate when mixed in a paint.

BROWN PIGMENTS

The carefully controlled heating of various naturally occurring iron-containing clays furnishes the brown pigments known as burnt *sienna,* burnt *umber,* and burnt *ocher.* The iron hydroxides are more or less converted to the oxides. The umbers contain the brown manganic oxide as well as the iron oxides. These are all very permanent pigments and very suitable for both wood and iron. *Vandyke brown* is a native earth of indefinite composition, containing oxide of iron and organic matter.

TONERS AND LAKES

Toners[1] are insoluble organic dyes that may be used directly as pigments because of their durability and coloring power. Lakes result from the precipitation of organic colors usually of synthetic origin upon some inorganic base.

Toners, or organic dyes, are employed in many colors. Some typical examples are given here. Para red is formed by diazotizing *p*-nitroaniline and coupling it with β-naphthol. Toluidine toner, a better and more expensive red pigment, is made by diazotizing *m*-nitro-*p*-toluidine and coupling it with β-naphthol. Hansa yellow G is manufactured by diazotizing *m*-nitro-*p*-toluidine and coupling it with acetoacetanilide.

The *lakes* are really dyed inorganic pigments. The inorganic part or base consists of such an extender as clay, barite, or blanc fixe and aluminum hydroxide. The organic dye may be either precipitated onto an already existing base, such as clay or barite suspended in solution, or both the dye and the base may be coprecipitated as onto blanc fixe or aluminum hydroxide. Both toners and lakes are ground in oil or applied like any other pigment. Both should be insoluble not only in water to resist washing away, but in oil to prevent "bleeding." As the latter property is not so easy to attain, an old color frequently will run or bleed into a new coat of another color. This can be prevented by painting over the old color a paint containing as a pigment an absorptive black or a metallic pigment like flake aluminum. However, the toners and lakes are very useful and beautiful pigments for paints and inks.

METALLIC POWDERS

In surface coatings, flaked or finely powdered metals[2] and alloys have come into wide application. This is not only for their appearance as pigments but in many cases for their chemical or anticorrosion effect. Among such metallic substances, bronze and aluminum powders have been employed for years in lacquers. In recent years aluminum flake, or powder in suspension in various media, has given excellent results as a light-reflecting pigment as well as a primer coat. On iron and steel to retard corrosion, pigments containing zinc dust or *powdered* zinc dust and zinc oxide have been demonstrated to possess real value. This latter is also true of powders of lead and lead alloys.

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[1] MATTIELLO, *op. cit.*, vol. 2, pp. 3–286; CALLAHAM, *op. cit.*

[2] MATTIELLO, *op. cit.*, vol. 1, pp. 555–612.

PIGMENT EXTENDERS

There are a number of different substances that may be added to paints as fillers or extenders[1] for the purpose of giving a thicker paint film, providing better weathering properties, furnishing a base for the real pigment, or reducing the cost of the pigment (see Tables 2 and 5). These extenders should not be viewed as adulterants. Quoting from Lewis, Squires, and Broughton,[2]

> The properties of such a (paint) film can be still further improved by incorporating a certain percentage of far coarser pigments, which by themselves are practically worthless—the so-called extenders. This calls to mind the well recognized principle of mixing in the case of materials such as concrete, where a mixture containing coarse, skeletal particles has the voids between these filled with progressively finer particles and the whole mass ultimately bonded together by a suitable matrix. The presence of 10 to 20 per cent of extenders in a paint, rather than being an indication of adulteration, may add materially to quality.

Barium sulfate, in the natural crystalline form of barite but finely ground or in the precipitated form of blanc fixe, is one of the most important of the extenders. Finely ground calcium carbonate, sometimes called *whiting*, is another. Ordinary silicon dioxide, when finely divided, makes a good filler. Magnesium silicate is also widely used—the trade names being *asbestine* and *talc*, the latter being finely ground soapstone.

OILS

Although, in the organic surface-protective industries, oils do serve as vehicles for the carrying of the pigments, their chief function is to form or to help form the protective film. For this, reactive oils[3] are necessary, such as those which are drying or semidrying.

Drying Oils	*Semidrying Oils*
Tung oil	Soybean oil
Oiticica oil	Menhaden oil
Linseed oil	Other fish oils
Perilla oil	
Dehydrated castor oil	

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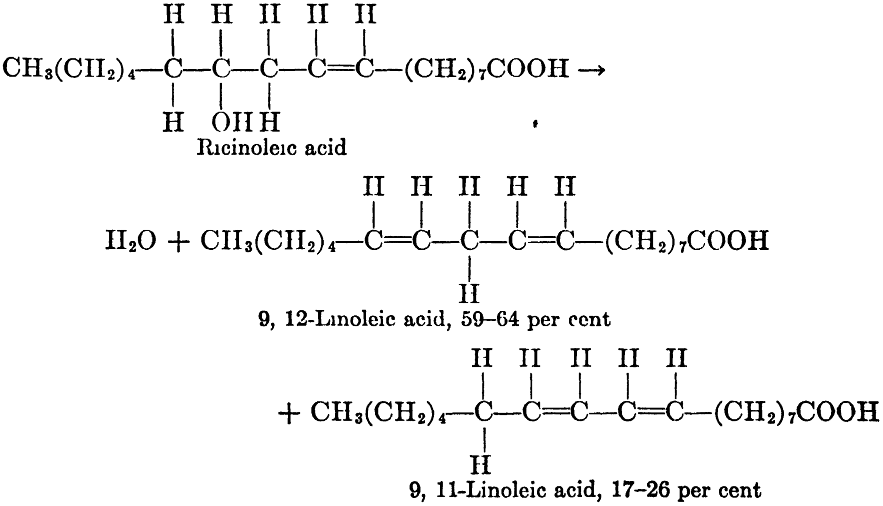
[1] MATTIELLO, *op. cit.*, vol. 2, pp. 427–479; HARNESS, Natural Mineral Paint Extenders, *U.S. Bur. Mines, Inf. Circ.* 7264, Washington, 1943.

[2] LEWIS, SQUIRES, and BROUGHTON, "Industrial Chemistry of Colloidal and Amorphous Materials," p. 326, The Macmillan Company, New York, 1942. By permission.

[3] MATTIELLO, *op. cit.*, vol. 1, pp. 57–174; KILLEFFER, Drying Oils, *Ind. Eng. Chem.*, **29**. 1365 (1937).

The drying or the hardening of these oils involves chemical reactions, rather complex but including oxidation as the initiating step. Some polymerization also occurs, and much cross linkage. Those oils that exhibit this phenomenon of drying to a film possess olefinic unsaturation. For example, the acids of linseed oil contain 18 per cent of oleic acid, 37 per cent of linoleic acid, and 40 per cent of linolenic acid. In drying, these oils at the first stage absorb oxygen from the air forming peroxides at the olefinic bonds. These still liquid products partly decompose, giving the volatile oxidation products, but mainly change in the next stage of the reactions, by cross linkages into the solid though still elastic films. This last reaction is in all probability akin to resinification. In case of linseed oil, the solid, insoluble, but elastic film is called *linoxyn*. Such films are not permanent as the chemical reactions continue though at a much slower rate until, after the course of years, the film is entirely destroyed. Light, particularly ultraviolet, catalyzes these reactions and one of the functions of the pigment in surface coatings is to reflect the light away and thus to help preserve the film.[1]

To supply some of the demand for drying oils, a dehydrated castor oil is manufactured by heating castor oil in a vacuum and in the presence of dehydrating catalysts, as alumina, fuller's earth, silica gel, or sulfuric acid. About 5,000,000 lb. were so made in 1940. The oil loses water amounting to about 5 per cent of its weight and forms a product of greater unsaturation. The reaction[2] is probably as follows:



$$CH_3(CH_2)_4-\underset{H}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\overset{H}{C}=\overset{H}{C}-(CH_2)_7COOH \rightarrow$$

Ricinoleic acid

$$H_2O + CH_3(CH_2)_4-\overset{H}{C}=\overset{H}{C}-\underset{H}{\overset{H}{C}}-\overset{H}{C}=\overset{H}{C}-(CH_2)_7COOH$$

9, 12-Linoleic acid, 59–64 per cent

$$+ CH_3(CH_2)_4-\underset{H}{\overset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{H}{C}=\overset{H}{C}-(CH_2)_7COOH$$

9, 11-Linoleic acid, 17–26 per cent

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[1] A fuller summary of researches in this matter is presented in Leighou, *op. cit.*, pp. 545, 560–564; LEWIS, *et al.*, *op cit.*, pp. 323–326.

[2] PRIEST and MIKUSCH, Composition and Analysis of Dehydrated Castor Oil, *Ind. Eng. Chem.*, **32**, 1314 (1940); MATTIELLO, *op. cit.*, vol. 1, p. 115.

It was earlier thought that the 9,11-linoleic acid, with its conjugated double bonds, was formed in the larger amount, but this recent investigation shows the other isomer to exist in the larger quantity. The composition of the fatty acids in the thoroughly dehydrated castor oil, analyzes as follows:

	Per Cent
Saturated acids	0.5– 2.5
Hydroxyl acids	3 – 8
Oleic acid	7.5–10.5
9,12-Linoleic acid	59 –64
9,11-Linoleic acid	17 –26

VARNISHES

A varnish may be defined as a homogeneous fluid, which, when applied by any suitable means in a thin layer . . . dries either by evaporation of the volatile solvent, or by combined evaporation of the volatile solvent and oxidation of component oils and resins to a more or less impervious elastic film of varying degrees of hardness and of generally good weather resisting properties.[1]

Varnishes fall into two general classes: oil varnishes and spirit varnishes. To these is sometimes added a third class, the japans. Oil varnishes are solutions of one or more natural or synthetic resins in a drying oil and a volatile solvent. The oil reduces the natural brittleness of the pure resin film. Spirit varnishes are likewise solutions of resins, but the solvent is completely volatile and nonfilm-forming. Table 6 gives a concise summary of the ingredients of the various varnishes.

Manufacturing Procedures.—The processes for the various types of varnishes may vary considerably depending upon the types of solvent and of gum resin added.

The *oil varnishes* may be considered solutions of a resin, natural or synthetic, in a drying oil to which have been added a drier and a thinner. The preparation of this type is begun by heating the resin hot in kettles on wheels or in large stand pots. During this operation, frequent stirring is maintained, and the vapors are removed by an exhaust fan. When the proper consistency is reached, the oil, which has been preheated, is added to the liquid resin whereupon a smooth solution results. After the varnish is below the flash point of the thinner, the thinner and drier are blended in. The product is allowed to cool overnight and is then run through the clarifier (similar to a cream separator) to remove any foreign particles. A period of aging in large tanks completes the process.

The *spirit varnishes* are solutions of resins in volatile solvents only, usually either methanol or alcohol. Spirit varnishes dry the most rapidly but are liable to be brittle and eventually crack and peel off unless suitable plasticizers are added. The preparation of these products involves active stirring and sometimes heating to bring about the desired solution. The most important example of a spirit varnish is shellac or a solution of the resin shellac in methanol or alcohol. Not being pigmented, varnishes are less resistant to light than are paints, enamels, and pigmented lacquers. They furnish, however, a transparent film which exhibits the texture of the surface coated.

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[1] THORPE, "Dictionary of Applied Chemistry," 3d ed., vol. 7, Longmans, Green and Company, New York, 1930.

TABLE 6.—VARNISH CONSTITUENTS
(Enamel if pigmented)

Class	Ingredient	Function
1. Film-forming materials	*Resin, natural:* Shellac, insect secretion Rosin, residue from balsams of certain pines Dammar, recent fossil resin Copal. fossil resin Kauri, old fossil resin *Resin, synthetic:* Phenol-aldehyde, oil soluble Alkyd or glyptal Urea-formaldehyde Cumar *Drying oil:* Linseed oil Tung oil	To form protective film upon evaporation of solvent or upon drying of any varnish oil used
2 Solvents or vehicles	*Drying oil,* above *Volatile solvent:* Turpentine Naphtha Kerosene Alcohol Methanol Isopropyl alcohol	To dissolve film-forming materials
3. Driers	Pb, Mn, Co resinates, linoleate or oleates	To hasten hardening or drying of any varnish oil employed
4. Diluents or thinners	Solvent naphtha (coal tar) V. M. & P. naphtha (petroleum)	To aid in application by reducing viscosity and to give a thinner coat

Japans are of two types: painter's japans and decorative japans. The former, added to paints to give more luster, consist of a resin dissolved in a drying oil to which are added driers and thinners. The latter are opaque varnishes to which asphaltum or some similar material has been added for color and luster. They may be subdivided into baking, semibaking, and air-drying japans according to their method of application.

Resins.—The original resins[1] used were the *copals* which consisted of fossil gums from various parts of the world. Another natural but present-day resin widely employed is that from the pine tree, or *rosin* as it is called. When a plant exudes these products, they are called *balsams* and, upon evaporation of the volatile constituents, yield the resin. Thus the long-leaf, yellow, or hard pine of the Southern states upon proper incision yields a balsam which after distillation gives turpentine and a residue called *rosin*. This latter product is essentially abietic acid (see Chap. XXXII). Most of the natural resins that have been employed are fossil resins that have been buried and gradually changed by the centuries. From the rosin of present days, these resins[2] reach back through dammar, copal, and kauri resins to the oldest of the fossil resins, amber. Some resins like kauri and copal are so ancient that they have changed to insoluble products and must be partly depolymerized by heat before they can be dissolved or blended with the hot oils and other constituents in the varnish kettle. An important resin of the present day is *shellac* or *lac resin*. This, unlike the others, is the product of animal life, from a parasitic female insect (*coccus lacca*) which, feeding upon certain trees in India, secretes a protective exudate that eventually coats the twigs, furnishing the *stick lac*. This is collected and purified to the shellac of commerce by rolling, crushing, separating, washing, and bleaching.

Overshadowing these natural products, are the more recently introduced synthetic resins (see Chap. XXXV). The *phenolic resins* (phenol-formaldehyde) were the first of these to be supplied and are still in wide use as they are very resistant to water and many chemicals. In order to make these materials soluble in the oils and solvents in common use in the varnish industry, it is necessary to modify them. This may be done either by fluxing them with softer materials such as ester gum, or by controlling the reaction by choosing a para-substituted phenol and thus stopping the reaction before a final insoluble, infusible product is obtained The *alkyd resins* (glycerine-phthalic anhydride) are also important to a great ~~extent in~~ the industry today as they yield films that are tough, nonyellowing, and stable. *Ester gum*, the product of the esterification of the abietic acid of rosin with glycerine, is another one of the important raw materials for making varnish. Some of the newer resins that may be mentioned in this connection are the coumarone-indene type, the urea-formaldehyde types, and the melamine resins. The synthetic resins have numerous advantages over the naturally occurring types such as superior resistance on exposure to weather and chemicals and ability to be baked more rapidly at higher temperatures.

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[1] MATTIELLO, *op. cit.*, vol. 1, pp. 175–498.

[2] For a fuller account see Leighou, *op. cit.*

ENAMELS AND JAPANS

Enamels are pigmented varnishes and are consequently more resistant to sunlight. Some enamels can be brushed or sprayed on the surface while others are finally hardened by baking, the latter being very durable.

Japans are very closely related to enamels, being pigmented with asphaltum or stearin pitch. For the desirable deep-black japans some carbon black is added. These japans are based on a heavily lead-bodied oil, made by cooking linseed oil and litharge for about 5 hr. at around 230°C. The product is almost a solid mass and is called *lead oil.* To this are added the asphaltum and any necessary thinners (kerosene). These japans[1] are applied and baked at 200°C. for a few hours. The japans are very useful for such products as bicycles, bedsteads, and electrical devices.

LACQUERS

Lacquers are solutions in organic solvents of such film-forming materials as nitro-cellulose with or without the addition of natural or synthetic resins. Table 7 summarizes the constituents of lacquers. Clear lacquers upon the addition of a pigment become lacquer enamels or simply pigmented lacquers. Naturally the latter, because of the light-reflecting pigment, are more permanent to weather. Lacquer is a fairly recent addition to the organic surface-protecting industries, but it has had a phenomenal growth owing to a number of factors such as the enormous quantity of nitrated cellulose recovered from the breakdown of shell of the First World War and the commercial production of a number of new and suitable solvents, both coupled with the development of the automobile industry.

The nitrated cellulose of the variety used as a propellant explosive in shell is not the ideal film-forming material, but it was very cheap (as recovered from unused shell) and abundant. However, nitro-cellulose of any variety upon solution in suitable solvents is too viscous to allow sufficient to be dissolved to furnish a lacquer of requisite film thickness and yet be limpid enough for spraying or brushing. The early films were also too brittle and did not adhere well.

The invention of means to reduce viscosity laid the foundation for the rapid development of lacquer. This is now carried out by heating nitro-cellulose of the nitrogen content to ensure desired solubility, with water in the liquid phase. This is done at about 130°C. by pumping the aqueous suspension of nitro-cellulose through a steel pipe against the pressure of a standpipe at the exit. Such a procedure is safer than the old method of heating a large amount of water and nitro-cellulose in a steel tank autoclave. Chemically in all probability, the long-chain cellulose ester molecules are degraded by hydrolysis to produce this lowering of viscosity. The choice of the solvents also has an effect on the viscosity, this being reduced if a solvent is selected which in itself does not dissolve the nitro-cellulose but yet mixes with the other organic liquids. This is called *desolvation*.[1]

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[1] Many formulas are given by Bennett, "Chemical Formulary," vol. 1, p. 240, Chemical Formulary Co., Brooklyn, 1933.

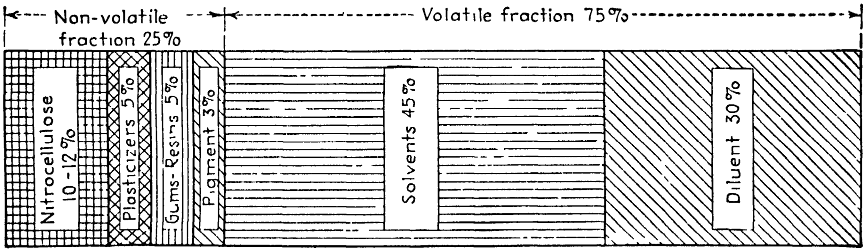

FIG. 7.—Approximate composition of lacquers. [*Ind. Bull.* 17, *No.* 7, *New York State* (1938).]

Lacquer formulation is very complex. By reason of the large number of constituents available now numbered in the hundreds, lacquers eminently and specifically suitable to a wide variety of different objects whether of metal or of wood are available. These lacquers have greatly decreased the cost of finishing automobiles and given a longer lasting job. This saving has been passed on to the consumer.

Figure 7 indicates roughly the composition of a typical nitro-cellulose lacquer. There exist considerable variations for individual lacquers. No one can efficiently fit a lacquer formula to a specific application without wide training, deep knowledge, and years of experience in this field.[2]

The ordinary lacquer consists of five or six classes of ingredients as tabulated in Table 7, each of which has a definite function and also augments the properties of the others, thereby giving a finished product of desired characteristics. The classes of ingredients and their functions are as follows:

1. Among *film-forming bases*, nitro-cellulose or cellulose acetate gives waterproofness, hardness, and durability to the coating. The nitrocellulose or, as it should be called, the *cellulose nitrate*, is an ester of cellulose made by the reaction of mixed nitric and sulfuric acid on cotton linters

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[1] LEWIS, *et al.*, *op. cit.*, p. 318.

[2] MATTIELLO, *op. cit.* See all volumes.

TABLE 7.—LACQUER CONSTITUENTS

Class	Ingredients	Function
1. Film-forming or basic materials	*Cellulose derivatives:* Nitro-cellulose Cellulose acetate Ethyl cellulose	Cellulose derivatives to furnish waterproofness, hardness, and durability
	Resins and gums: Ester gum Dammar Copal *Synthetic resins:* Phenol-aldehyde Alkyd	Resins, natural and synthetic, to improve retention of original gloss, adhesion, and water resistance
2. Pigments—omitted in clear lacquers	See Table 2	To impart pleasing color and to improve resistance to light
3. Solvents	*Esters:* Ethyl acetate (rapid) Butyl acetate (slow) Amyl acetate (slow) Ethyl lactate (slow) *Ketones:* Methyl-ethyl ketone (rapid) Cyclohexanone (slow) *Ethers:* Cellosolve (slow) *Alcohols:* Ethyl alcohol (rapid) Butanol (slow) Amyl alcohols (slow)	To dissolve the film-forming substances and to suspend the pigments. Rate of evaporation and solvency is governed by choice of the various solvents. "Rapid" and "slow" refer to rate of evaporation. Ethyl alcohol is a latent solvent becoming an actual solvent in presence of esters and ketones. Usually mixtures give best results
4. Diluents	*Coal-tar products:* Toluol Benzol Solvent naphtha *Petroleum products:* Petroleum naphtha V.M. & P. naphtha	To reduce viscosity and cost
5. Plasticizers	Castor oil Dibutyl phthalate Tricresyl phosphate	To reduce film brittleness and to improve adherence
6 Stabilizers	Urea β-Naphthylamine	To stop decomposition of nitro-cellulose by absorbing acid products

as is described in Chap. XXII. The degree of nitration is closely controlled to give a product with the desired range of solubility. Cellulose acetate, the acetate ester, is made in a similar manner, with acetic anhydride replacing the nitric acid (*cf.* Chap. XXXIV). The acetate has an advantage over the nitrate in that the film formed is not flammable. The nitro-cellulose comes to the lacquer manufacturer in the form of a white solid moistened with about 30 per cent ethyl alcohol. The solvents, plasticizers, and diluents are blended in using mechanical agitation. The lacquer solution is clarified either by filtration or centrifuging. In case the lacquer is to be colored, the pigment is ground with a small amount of the solvent in a buhrstone or ball mill before being incorporated with the rest of the constituents. Other film-forming materials are the resins, both natural and synthetic. These are added to supplement the cellulose derivatives and to improve the over-all properties[1] of the film.

2. *Pigments* have been presented in the earlier part of this chapter.

3. *Solvent formulation*[2] is a very complex subject. Bogin lists the following factors to be considered:

1. Rate of evaporation.
2. Solvency relations.
3. Effect on the viscosity of solution.
4. Compatibility with resins and other ingredients.
5. Blushing behavior.
6. Flow and orange peel.
7. Stability.
8. Odor, purity, availability, etc.

As Table 7 points out, mixtures are the rule, the choice of constituents being governed by the film-forming materials and the rate of evaporation desired. It should be noted that the *drying of lacquers is not an oxidation but an evaporation,* with the properties of the film dependent not only on the nature of the film but upon the conditions of the evaporation. Thus blushing may result in an improperly formulated lacquer; this is a whitish or milky appearance in the film caused by the too rapid evaporation of the solvents and diluents with consequent cooling of the film 30 to 40°F. below the temperature of the atmosphere. This causes a condensation of moisture upon the lacquer and results in a milky aqueous emulsion. Upon drying, the water phase is occupied by air, resulting in the same milky[3] appearance.

4. The *diluents* are of great importance in reducing cost. Tolerance of the various solvents for these diluents is an important property in the

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[1] See the various chapters devoted to particular resins in Mattiello, *op. cit.*, vol. 1.

[2] BOGIN, Lacquer Solvents and Formulation of Solvent Mixtures, Chap. 27, in Mattiello, *op. cit.*, vol. 1. Extensive tables and curves are included, giving evaporation rates, tolerances, and other pertinent chemical and physical properties.

[3] BOGIN, *op. cit.*, pp. 686–694.

choice of the original solvents. The diluents have a real dissolving effect on any gums used.

5. The original nitro-cellulose film was far too brittle for practical application. The *plasticizers* remedy this and also improve adhesion. Dozens of plasticizers are available to the lacquer formulator. These are really *very high boiling* solvents of great chemical stability.

PRINTING INKS

Printing inks consist of a suspension of pigments in a drying oil or petroleum oils. Other ingredients may be various resins, waxes, gums, water-insoluble soaps, driers, and antioxidants. Printing inks have a wide variety of compositions and a large variation in properties.[1] This is because of the great number of different printing processes and types of papers employed. A very general classification of printing processes would include typographic, lithographic, and intaglio.

The vehicles employed in inks are the drying oils or petroleum oils and resins. The newer types based on synthetic resins are finding great favor because they are quick drying, and their working properties are excellent.

The usual paint pigments are also employed in printing ink, although some of the metallic oxides are too coarse and gritty for this use. The driers described under Paints are the ones used in inks as well. Antioxidants are used to counteract pigments which are natural oxidation catalysts. Guaiacol is a typical example.

The actual manufacture of printing inks consists in grinding the pigment in a small amount of vehicle and then mixing in the remainder of the constituents. Details of manufacture will vary greatly with the type of ink being produced.

ARTIFICIAL LEATHER

An industry closely allied to the lacquer industry is the manufacture of artificial leather.[2] Artificial leather consists of multiple layers of pigmented nitro-cellulose lacquer deposited upon a cloth backing, dyed the same color, and embossed to simulate the appearance of leather. Eighty million square yards of this material were produced in 1937 by 25 plants; the value of the product was $24,000,000.

The basis of this artificial leather is a cotton cloth which varies in grade according to the product being made. The first step is to remove any loose threads and knots that might cause bumps in the finish. The cloth then runs into a series of dye vats where it is colored the shade of the leather being made. The drying of the dyed fabric is carried out on a series of steam-heated rolls, followed by a tunnel drier (see Fig. 8).

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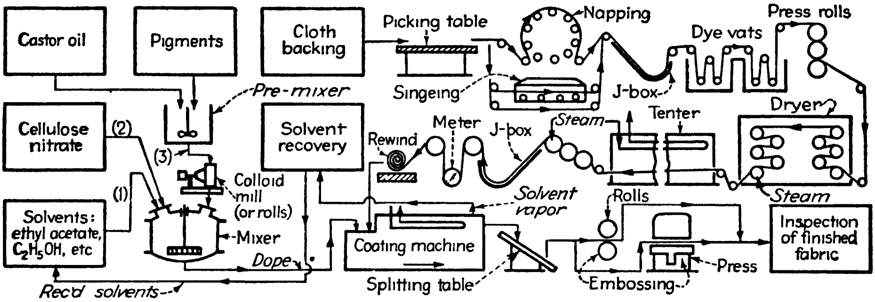
[1] For a complete description of inks see Ellis, "Printing Inks," Reinhold Publishing Corporation, New York, 1940.

[2] For details of manufacture see Clark, Leather Cloth from Chemicals, *Chem. & Met. Eng.*, **47**, 544 (1940).

At the same time the cloth is being dyed, the coating solution or "dope" is being prepared in another part of the plant. The ingredients of this substance are nitro-cellulose, castor oil, pigment, and solvents. The castor oil and pigment receive a preliminary mix and are fed to the dispersion mills, which consist of two circular plates, set close together and rotated in opposite directions. This dispersion, plus the nitro-cellulose, more castor oil, and the solvents (a mixture of ethyl acetate, naphtha, and ethyl alcohol) are all mixed in large tanks to give the dope.



Dope consists of 60 percent solvents, 40 percent pyroxylin Solvent fraction may consist, for example, of 30 percent ethyl acetate, 40 percent ethyl alcohol and 30 percent naphtha "Solids" fraction may contain, for example, 25 percent pigment, 25 percent cellulose nitrate and 50 percent castor oil

FIG. 8.—Pyroxylin coated fabrics.

Care must be taken in these operations to avoid fires and explosions due to the flammability of the nitro-cotton and solvents.

The fabric is coated with the dope in large automatic machines, the thickness of the layer being regulated by doctor knives. These machines are completely enclosed for solvent recovery, steam-heated cylinders causing the evaporation. From 3 to 20 layers of the nitro-cellulose (pyroxylin) material are added before the product is finished. Large embossing roll presses or bed presses put on designs such as resemble buckskin or pigskin.

The vapors being drawn off the coating machines contain from 0.7 to 0.9 per cent solvents. These are cooled and the solvents removed by passing through activated carbon absorbers.[1] When the carbon is 75 to 80 per cent saturated, the solvents are driven off with steam, the vapors condensed, separated, and rectified.

A product similar to this is artificial suède, made by spraying rubberized fabric with rubber cement and then spreading cotton fibers over it. Beating to make the fibers stand up and then vulcanization complete the process.

[1] See Chap. IX.

LINOLEUM

Linoleum, widely used for floor covering, was introduced in England in 1860. It consists of a mixture of linoxyn or oxidized linseed oil, pulverized cork, wood flour, pigments, and colors, all spread in a uniform layer on canvas or burlap backing, the surface of which may be printed in patterns of different colors. The oxidizing of the linseed oil is effected by exposing it in thin films to air. The entire surface is afterward coated or waterproofed with an oil paint. With inlaid linoleum, the pattern goes right through the fabric, the different sections being pieced together and then passed between heated rolls.

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CHAPTER XXV

LEATHER, GELATINE, AND GLUE

The chemistry and engineering behind the leather and leather-tanning industry are so complex that scientific control in this industry has developed comparatively slowly. The skins and bones of animals and their products—leather, gelatine, and glue—are mostly colloidal materials and have almost indefinable properties, about which too little is known. The raw skin consists of a number of different complex proteins which vary in structure in different animals and even vary in different parts of the same hide. It has been said by Claflin, "Tanning will ever be an art so long as one animal differs from his fellow and one hide from another." The complexity of the art of leather manufacturing is enhanced by the large number of active substances that affect the skins—enzymes, bacteria, alkalies, acids, tannins, tannin substitutes, oils, fats, and salts. The leather industry is constantly searching for new chemicals with which to make better leathers at a cheaper price. It is already a large consumer of many chemicals (see Table 4).

LEATHER

Historical.—Leather is one of the oldest of the commodities on the present-day world market. It has been called "the most historic of useful materials." The art of leather manufacturing from hides and skins antedates, by centuries, any of man's scientific knowledge of chemistry. Specimens of ancient Egyptian leather have been found which are claimed to be at least 3,000 years old. The color and strength of this leather are remarkably unimpaired. Judging from these well-preserved leather products, the origin of the technique must have antedated this time by many centuries. The original primitive methods for preservation of skins probably consisted of simply drying them in air and sunlight. Later the preservative effects of different oils were noted. Still later probably, the accidental discovery of the tanning effects of leaves, twigs, and barks of certain trees soaked in water were observed. It is believed that until 50 years ago the development of the leather industry was chiefly the result of rule-of-thumb discoveries, since it is only within recent times that any of the theory of leather tanning and dressing has been given in chemical terms.

Probably the greatest modern advancement in the leather industry has been the discovery and application of the chrome process of tanning which was first used approximately 35 years ago. Because of the results of this process, 90 to 95 per cent of the world's output of upper shoe leather is now chrome-tanned, this process having almost completely replaced vegetable tanning methods for this type of leather. The chrome process has greatly speeded up the tanning operation. It also gives increased strength. Vegetable tanning takes 4 to 5 months while the chrome process has reduced this interval to as many weeks. The chief use of vegetable tanning at present is in the tanning of heavy leathers such as sole leather or leather belting; consequently, this old historical process is still widely employed and produces about half of the leather manufactured.

Economics and Uses.—The chief consumer of leather is the shoe industry. The United States produces about 40 per cent of the world output of leather boots and shoes, and the 1939 output is estimated at 435,000,000 pairs by 1,070 shoemaking establishments in the United States.[1] The accompanying tables show the types of leather and raw materials, the uses of leather, and the extent of the leather industry in the United States.

The discovery and manufacture of artificial leather have offered mild competition to the leather industry, but its production is still very much below that of leather. In 1937, the total value of leathers produced in the United States was $372,458,000 compared to $27,876,000 for the value of artificial leather.

ANIMAL SKINS

The United States is able to produce most of its own hides and skins for leather production. South America is the chief source of hides imported; the Argentine hides are usually of very good quality. Tech-

TABLE 1.—LEATHER AND THE LEATHER INDUSTRIES IN THE UNITED STATES[a]

Census year	No. of establishments	No. of wage earners (average for year)	Thousands of dollars			
			Wages	Cost of materials, fuel, purchased energy, etc.	Value of products	Value added by manufacturer
1933	3,265	282,000	$222,487	$544,737	$ 996,773	$452,036
1935	3,506	310,755	279,740	694,293	1,224,431	530,139
1937	3,364	331,955	311,293	899,469	1,491,513	592,043
1939	3,508	327,663	294,290	805,911	1,389,514	583.602

[a] "Manufactures, 1939, Leather and Leather Products," 16th Census of the United States, U.S Department of Commerce, 1941.

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[1] "Manufactures, 1939, Leather and Leather Products," 16th Census of the United States, U.S. Department of Commerce, 1941.

TABLE 2.—TYPES AND QUANTITIES OF RAW MATERIAL FOR LEATHER[a]
(In thousands of the article specified)

Year	No of cattle hides	No of calfskins and kips	No. of goat and kidskins	No of sheep and lambskins
1933	17,115	13,049	44,312	33,881
1934	19,771	12,442	44,982	34,255
1935	21,932	14,140	48,250	38,465
1936	22,628	13,127	47,363	37,942
1937	22,380	12,027	46,554	34,232
1938	19,047	12,991	31,905	28,941
1939	22,095	14,027	40,419	39,384
1940	21 013	11,387	37,697	37,920
1941	28,121	13,098	45,373	51,915

[a] "Statistical Abstract of the United States," 1942, p 925, Government Printing Office, Washington 1943

TABLE 3.—LEATHER PRODUCTS, 1939[a]

Product	Quantity	Value
Sole and belting leather		
Oak, union, chrome sole, lb	201,020,540	$ 60,048,623
Horse sole, sq ft	3,959,564	938,286
Belting butts, curried, lb	6,106,808	3,660,983
Offal, lb	88,686,623	16,314,437
Harness leather:		
Union black, lb	1,335,222	386,668
Oak black and russet, lb	6,332,418	1,879,874
Bag, case, and strap leather, sq ft	21,244,790	4,888,314
Collar, skirting, and latigo leather, sq ft	9,413,569	2,333,751
Welting leather cattle, lb	7,932,912	2,490,555
Upholstery leather, finished:		
Whole-hide grains, sq ft	17,791,097	4,035,829
Splits, sq ft	10,192,511	1,170,642
Upper leather:		
Cattle, including kip sides, sq ft	362,920,748	66,458,157
Calf and whole kip, sq ft	123,139,939	34 482,079
Goat and kid, sq ft	141,410,030	26 514,759
Others, sq ft	63,828,160	8,873,216
Glove and garment leather		21,614,396
Fancy and bookbinding leather, sq. ft	26,406,914	5,571,693
Lining leather, sq ft	259,022,434	29,979,954
Miscellaneous leather, sq ft	108,613,183	30,717,221
Total		$322,359,437

Manufactures, 1939, Leather and Leather Products," 16th Census of the United States, U S Department of Commerce, 1941 nically, the term *hide* is applied to the skins of larger animals such as bulls, horses, cows, and oxen; the term *skin* refers to skins of goats, sheep, calves, and the smaller animals. Very often the term *kip* is used for the skins of animals smaller than a full-grown calf.

Animal skins are composed of two layers: the epidermis and the derma or corium. The epidermis, comprising about 1 per cent of the total skin, is the outer layer and consists chiefly of the protein keratin. The hair, which grows through both the derma and the epidermis, is also largely keratin. The derma is the leather-forming part of the skin and consists mainly of the proteins collagen and elastin. This layer is dense and chemically resistant, thus allowing the epidermis to be readily removed by chemical means. Hot water, however, causes a slow solubilization by hydrolysis of the collagen to produce gelatine. The elastin is not affected by this treatment.[1]

TABLE 4.—ESTIMATED CONSUMPTION OF CHEMICALS IN LEATHER MANUFACTURE[a]

Chemical	Tons
Sodium sulfide	11,000
Lactic acid	5,000
Tanning extracts	170,000
Sulfuric acid (50°Bé.)	3,000
Salt	350,000
Sodium dichromate	4,000
Sodium thiosulfate	13,000
Borax	2,000
Oils and fats	11,000

[a] *Chem. & Met. Eng.*, **44**, 584 (1937).

MANUFACTURE

Unit Processes and Unit Operations.—Figure 1 shows the necessary steps in the manufacture of leather.[2] These steps may be broken down into the following *unit operations* (Op.) and *unit processes* (Pr.):

The skins are opened, examined, and, if of foreign origin, disinfected. The hoofs, ears, tails, etc., are trimmed off (Op.).

The skins are water-soaked in pits for two days (Op.).

The soaked skins are scraped with dull knives to remove any flesh (beaming) (Op.).

They are partly dehaired and treated with a lime and sodium, arsenic, or calcium sulfide solution for 10 days (Op. and Pr.).

Any hair remaining is removed by machine and hand scraping (Op.).

The clean, dehaired hides are treated with pancreatic enzymes for 2 days to soften the skin and remove the lime (bating) (Pr.).

After rinsing, the hides are ready for tanning (Op.).

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[1] LEWIS, SQUIRES, and BROUGHTON, "Industrial Chemistry of Colloidal and Amorphous Materials," The Macmillan Company, New York, 1942.

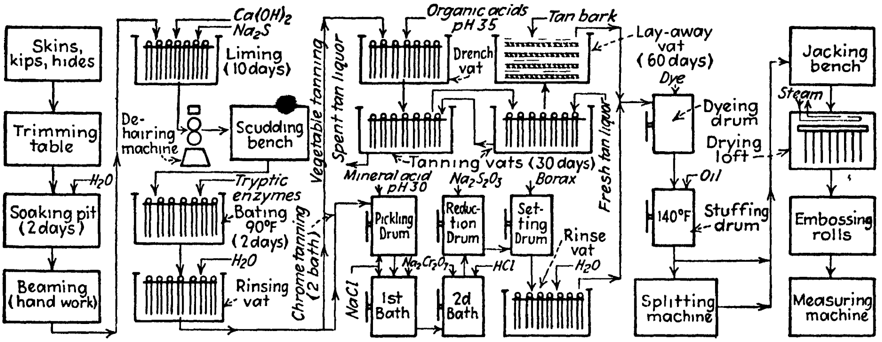
[2] Pictured flow sheet with more details, *Chem. & Met. Eng.*, **50**, No. 1, 112 (1943).

The two principal methods of tanning are shown in Fig. 1.

The vegetable tanning process consists of the following procedures:

The prepared skins are treated with organic acids to neutralize any residual lime (Pr.).

The tanning is carried out in several tanning baths starting very weak to prevent "casehardening" and becoming progressively stronger. This requires about 1 month (Pr.).



Hides	100 lb.
Lime	10 lb.
Na_2S	2 lb
Water	200 gal.

Vegetable Tan	
Lactic acid	1.2 lb.
Tan bark	20 lb.
Water	175 gal.

Chrome Tan	
HCl (30%)	25 lb
NaCl	20 lb
$Na_2Cr_2O_7 \cdot 2H_2O$	5 lb
$Na_2S_2O_3$	15 lb
Borax	2 lb.
Water	400 gal.

Dye	1 lb	To produce 125 lb vegetable tan or 80 lb chrome tan leather
Oil: Sole	2 lb	
Belting	8 lb	
Harness	20 lb	
Electricity	1 kw-hr	
Direct labor	2 man-hr.	

FIG. 1.—Leather manufacture.

The skins are then allowed to rest in a vat containing tanbark for 60 days (Pr.).

The chrome tanning process is somewhat different from the tannin process as indicated in Fig. 1.

The prepared skins are pickled in a bath of salt and sulfuric acid (Pr.).

The pickled hides are soaked with a solution of sodium dichromate (Op. and Pr.).

The dichromate saturated skins are treated with sodium thiosulfate in the reduction drum (Pr.).

TABLE 5.—COMPARISON OF SKINS AND LEATHER

	Skins or hides	Leather
Pliability	Soon lose pliability and become hard and brittle	Retains pliability
Permanence	Putresce very quickly	Extremely permanent, not attacked by bacteria
Water resistance	Absorb water and are permeated easily by it	Possesses great resistance to water
Boiling water	Are converted to gelatine by hydration	Attacked with great difficulty
Mechanical strength	Fairly good	Very good

The chrome salt is set on the fibers by adding borax to the skins in the settling drum (Pr.).

After washing, the leather is ready for the finishing operations (Op.). Finishing operations are identical for both methods of tanning.

The tanned hides may be dyed (Pr.).

The leather is stuffed with oil (Op.).

The leather is split to produce a thinner, more supple product (Op.).

Gloss is developed on the surface of this leather by ironing and jacking the leather with a glass cylinder (Op.).

The jacked leather is dried (Op.), embossed (Op.), and measured (Op.).

In industrial application these unit processes and operations are complicated and require experienced men to carry them out. Each important operation or process is given more detailed presentation on the next few pages. The results are tabulated in general in Table 5. However, leather has an outstanding extremely valuable property that is not duplicated by many of its substitutes, namely, its great permeability to air and moisture and therefore its ventilating property.

Preservation and Disinfection of Skins.—As the raw skins, after flaying, decay very readily, some method of preservation must be used to store them safely until the first tanning operation. Bacterial action and hide disintegration are usually prevented by the use of common salt, sodium sulfate, phenol, or sodium bisulfite. Care should be taken to prevent salt stains on the hides which are apparently due to the combination of some of the skin proteins with iron that might be present in the salt. In tropical countries, such as India or Java, very often the most economical method of preserving skins is drying them, which reduces the weight of skin by about 55 per cent. Very often the two preservative methods are combined. Many times irregularities in the stretch, tear, grain, and tensile strength of a leather may be traced to the curing and storage conditions, such as salting, after putrefaction has begun. The salting is usually done by spreading salt over the flesh side with a shovel and storing the hide so as to permit the brine to drain.[1] After 24 hr. the salt content is approximately 12 per cent by weight with a final maximum salt content of approximately 15 per cent, much water being lost with some salt.

Preparation of Hides for Tanning.—The first step in the tanning process is the inspection of the hides for defects as they come into the tannery, cutting off of ears and ends, the cleansing of the hides from dirt, manure, and salt, and restoring the hide to a natural soft hydrated state by paddle washing, drum washing, or soaking in vats.

In the paddle method, the washing is done in a cylindrical wooden vessel usually about 9 ft. wide and 5 ft. deep, containing a rotor or paddle

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[1] WILSON, "The Chemistry of Leather Manufacture," Reinhold Publishing Corporation, New York, 1928.

5 ft. in diameter. This paddle operates at approximately 15 r.p.m. and will hold approximately 3 lb. of water per pound of hide. The equipment is cheap and easy to construct, uses little power, and is not so liable to injure the hides as is the drum method. The chief disadvantages are the necessary high ratio of water to hide and the required hand removal of the hides from the paddle.

In the drum method, a cylindrical wooden drum (cypress or fir), about 8 ft. in diameter and internally fitted with wooden pegs or shelves, is used. The drum is rotated and gives the hides a tumbling effect during washing. The chief disadvantage of this method is the danger of damage or rub marks on the hides.

The soaking and washing of the hides are quite important because if the hide is not properly "wet back," it will not respond properly to the different tanning operations. If the hide is oversoaked, it will be soft and below par. A properly soaked hide contains about 65 per cent of water. Very often disinfectants are added to the wash water to retard further putrefaction of the hides. A water temperature as low as possible with a pH of 6 or 7 is also recommended for the same reason.

Liming.—Liming is a means of loosening and removing the epidermis and hair from the hide and is usually done in wooden or concrete vats. The hides are tied or hooked together and placed in the vats containing water with 10 per cent of the weight of the hides in lime, and 2 per cent of the lime weight in sodium sulfide which acts as an accelerating agent. Arsenic sulfide and sodium hydroxide are also used as accelerating or "sharpening agents." The hides are moved ahead daily in a series consisting of three to seven vats, remain in each one a day, and then enter a fresher lime vat. These vats are drained and the lime charge renewed about every 2 weeks in the summer and every 4 to 5 weeks in the winter.

The epidermis and hair are chiefly composed of keratin. Keratin is a protein containing a cystine residue which is easily attacked by alkali. Lime attacks the disulfide link in the keratin and thus softens the hair and removes the epidermis. This action may be represented[1] as

$$\mathrm{R{-}S{-}S{-}CH_2R + H_2O \rightarrow RSH + RCH_2SOH}$$
$$\mathrm{RCH_2SOH \rightarrow RCHO + H_2S}$$

After the hides have passed through this series of lime vats, they are usually placed in a vat of warm water which tends to shrink them and permits the easier removal of the hair. The hair and epidermis are removed in a dehairing machine. The skins are brought in contact with a roller set with dull knife blades which rub off the loose hair and epidermis, as represented in Fig. 1.

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[1] LEWIS, *et al.*, *op. cit.*

Bating.—For centuries bating was one of the most mysterious processes carried out in the tannery and by far the most unpleasant. The old method consisted of placing the limed skins in a warm infusion of the dung of dogs or fowls until the plumpness of the skins disappeared. When pigeon or hen manure was used, the process was called *bating,* and when dog dung was used, it was called *puering.*[1] Later the investigation of the important organic constituents of the dung led to the use of artificial materials and the process became known as *bating.*

Just before immersion of the hides into the tanning liquor, they undergo the bating or deliming process which now uses ammonium sulfate or chloride as the deliming agent, and the enzyme pancreatin for the removal of certain proteins, mainly elastin, and for the improvement of the color of the grain. The ammonium salts dissolve the lime and thus regulate the pH of the solution so that the enzymes are activated.[2] Another important reaction in bating is that called *falling* or the reduction in the degree of swelling of the protein constituents of the limed skin previously swollen during the liming process.

Vegetable Tanning.—As has been mentioned previously, chrome tanning is for light leathers, and the chief use of vegetable tanning is for heavy leathers used for soles and belting. The active ingredients in vegetable tanning reagents consist of a class of complex organic compounds known as *tannins,* which are found quite abundantly in the vegetable kingdom. The chief sources that have attained commercial importance for supplying tannin for leather manufacture are barks, leaves, twigs, fruits, pods, and roots of various trees, shrubs, and plants.

One of the most important sources of tannin in the United States is the American chestnut tree which has been quite abundant in North Carolina, Virginia, Tennessee, and northern Georgia. Oak and hemlock extracts are probably among the best vegetable tanning reagents costing 10 to 11 cents per tanning unit, while chestnut and quebracho extracts may be bought for 5 to 6 cents. It is for this reason that they are sometimes used in preference to the former. The foregoing tanning extracts are often called *catechol* tannins since, on heating them, catechol is obtained. Tanning reagents from wattle trees, myrobolan nuts, and gambier trees are often called *pyrogallol* tannins because, on heating, they give pyrogallol.[3] Although a few tanneries still extract their own tannin from raw materials grown in neighboring districts, the manufacture of tanning extracts has now become a separate industry of considerable size. Approximately 70 per cent of the tannins used in the United States is imported from other countries. Table 6 shows the average consumption of various vegetable tannins in the United States.

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[1] ROGERS, "Industrial Chemistry," p. 1342, 5th ed., D. Van Nostrand Company, Inc., New York, 1931; WILSON, *op. cit.*

[2] BELL, Leather, *J. Chem. Education,* **19**, 340 (1942).

[3] WILSON, *op. cit.*

The open-vat leaching method is one of the oldest but perhaps still the most commonly used. The tannin-containing bark, wood, or other material is chopped into small pieces, shredded in a bark mill, and placed in leaching tanks equipped with false bottoms and heating coils and usually arranged in batteries of eight. The bottom of each tank is fitted with a pipe through which the liquor may be pumped from one tank to another. Leaching of the bark is accomplished by countercurrent extraction with water. The bark is then dumped and discarded. The fresh water enters at its boiling point and, by means of heating coils in the vats, the temperature can be controlled so that it cools slowly and is about 60°F. for the last leach.

TABLE 6—FOREIGN AND DOMESTIC TANNINS USED IN THE UNITED STATES[a]

	Million Lb, Average
Quebracho (Argentina)	87 2
Myrobolan (British India)	28 5
Wattle bark (South Africa)	19 8
Valonia (Turkey)	18 3
Lambier (Malay)	3 8
Gallnuts (China)	2 95
Dive dive (Venezuela)	0 35
Hemlock (U S)	1 34
Sumac (Sicily, U S)	7 77
Oak	Figures not available
Chestnut	

[a] HESSEL MURPHY and HESSEL Strategic Materials in Hemisphere Defense ' p 147 Hastings House New York 1942

Usually the extract is muddy and contains suspended insoluble matter The extract is then clarified by filter-pressing, settling, and decanting or centrifuging. The liquid is concentrated in vacuum evaporators or specially constructed vacuum driers.

Synthetic Tanning Agents.—Syntans are gaining in use, although vegetable tanning extracts are still widely employed. The synthetic materials usually consist of some sulfonic acid condensation product. For example, a tanning agent may be made by heating to boiling a mixture of a naphthalene-sulfonic acid, dihydroxy-diphenyl-sulfone, and water and formaldehyde, and neutralizing with alkali or water glass. Synthetic agents are also made by heating chloro-phenol with a sulfonic acid and formaldehyde.[1] In some cases sulfite-cellulose waste liquors are employed as tanning agents after the calcium salts have been removed by precipitation with sodium carbonate. However, they are usually used only as a pretreatment to be followed by other tanning reagents.

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[1] GRASSER, "Synthetic Tannins, Their Synthesis, Industrial Production, and Application," Crosby, Lockwood & Sons, London, 1922, SMITH, New Chemicals Used in Leather, *Chem & Met Eng*, **46**, **72** (**1939**).

Tannins are complex mixtures of glucosides of various polyphenols. Their action on skin is to combine with the protein. The tannins act as negatively charged colloids. The proteins in the skins are positively charged if in acid media. Thus the tannins neutralize the charge on the proteins and coprecipitation or combination of the tannins and proteins occurs. Other complex processes also take place. As the proteins have a negative charge when in alkaline media, it is necessary to neutralize all of the lime from the liming process before tanning. During the tanning process the tannins liberate sugars which are oxidized to acids and thus keep the liquor acidic. These changes may be represented schematically as follows:

$$\text{Skin} + \text{tannin} \rightarrow \text{leather} + \text{sugar}$$

$$\text{Sugar} \xrightarrow{\text{oxidation}} \text{acid}$$

After complete precipitation of the protein the aggregate has the capacity to absorb large quantities of the tannin. Skins may increase in weight as much as 300 per cent during the tanning operation. This combined and absorbed material fills up the holes and stiffens the leather.[1]

In tanning it is necessary to immerse the skins first in a weak tanning liquor in order to prevent complete plugging of the surface pores and subsequent poor penetration of the tannins through the skins by a strong liquor.

Vegetable tanning is usually done in wooden (red pine) vats 8 by 7 by 5 or 6 ft. deep which contain the tan liquors and hides. Since the hides remain in the liquor from 1 to 6 months, many vats are required, and they must therefore be cheap and durable. Hides first enter the oldest, weakest tanning liquors to avoid casehardening and pass successively through liquors of increasing strength until they leave the freshest and strongest liquor as fully tanned leather. The ratio of liquor to hide is kept as low as possible and is usually 6 to 4 lb. of liquor to 1 lb. of hide. The art in tanning lies in the careful selection and blending in the proper proportions of the various tannins so as to give the desired type and color of leather. Sometimes the hides are placed on rockers or paddles for the first 15 to 20 days to give them a gentle movement in the liquid, which tends to accelerate the tanning and make a more uniform leather.

Many attempts have recently been made to speed up the tanning time and to shorten the expensive and tedious aging and mellowing in tan liquors. Such schemes as immediate introduction of the hide into a strong tanning reagent, use of formaldehyde, use of different solvents, use of alternations of pressure and vacuum, and use of higher temperatures have all been tried, but it is claimed that a poorer fiber, grain, and yield are obtained by these means. The methods seem to have attained no great success.

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[1] Lewis, *et al.*, *op. cit.*

The water supply to a tannery is very important from both the quality and the quantity point of view. It is claimed that 2 parts of iron per 1,000,000 of water darken the tan liquor and have an adverse effect on the soaking and swelling of the hides. The following are figures on the water consumption in leather manufacture:

Soaking and washing	10 lb. water per lb. hide
Liming, total consumption	1.1 lb. water per lb. hide
Ratio, water to hide	5:1, owing to recirculation
Beaming machine	1.5 lb. water per lb. hide
Bating and soaking, total	8 to 10 lb. water per lb. hide
Ratio, water to hide	6:1
Vegetable tanning, total	1.5 lb. water per lb. hide
Ratio, water to hide	8:1
Chrome tanning, total	29 lb. water per lb. hide
Finishing	2.5 lb. water per lb. hide
Hair washing	1.5 lb. water per lb. hide
Total average consumption	About 30 lb. water per lb. hide using vegetable tanning and 48 lb. water using chrome tanning

Chrome Tanning.—The uppers of a pair of chrome-tanned leather shoes will outwear two or three pairs of a vegetable-tanned product. For this reason 90 to 95 per cent of the world's production of light leather is chrome-tanned.

In the chrome process, the combination of the chromium salts and hide fibers is much more rapid and takes place without the degree of swelling that occurs in vegetable tanning. Therefore, the chrome leather is more pliable and looser in structure. Fillers are usually added to give water-resistant properties. The chrome leather is characterized by high content of original hide proteins and mineral matter, and by low content of water-soluble materials.

The mechanism of chrome tanning has not been well established. The tanning liquor has the same electrical charge as the hide. Therefore, the mechanism of coprecipitation, as given under vegetable tanning, is not applicable. It is possible that the collagen forms a coordination compound with the chromium salts.[1]

Chrome tanning is usually subdivided into two processes: the one-bath process using sodium dichromate and the two-bath process using chromic sulfate. However, in each case, chromium salt is used in place of the vegetable tanning agent. The chrome liquor for the one-bath process is usually made by reducing an acidified solution of sodium dichromate by slowly adding a solution of glucose to it or by bubbling sulfur dioxide through the dichromate until the reduction is complete.

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[1] Lewis, *et al.*, *op. cit.*

$$Na_2Cr_2O_7 + 3SO_2 + H_2O \rightarrow 2Cr(OH)SO_4 + Na_2SO_4$$

In the one-bath process, after the hides have been pickled, they are placed in a rotating wooden drum or vat containing a concentrated solution of chromic sulfate (or chloride), and the drum is rotated 5 to 6 hr. until the tanning operation is complete.

Various modifications of the two-bath process are in use, but the process used in Fig. 1 serves as an illustration. After pickling, the hides are placed, successively, in two drums or paddle vats containing about 5 per cent of the weight of the hides in sodium dichromate solution with some hydrochloric acid and salt. The skins are allowed to remain in each liquor overnight and are then pulled out and allowed to drain. After an hour or two, the hides are placed in another paddle vat containing approximately 15 per cent of the weight of the hides in sodium thiosulfate. The hides are left in this liquor overnight, pulled out in the morning, and washed in a drum containing water. Borax is added to reduce the acidity of the leather to the desired extent.

In the chrome process, the properties and composition of the finished leather are greatly influenced by many factors that can be controlled during tanning. Such factors as salt concentration, temperature, agitation, time, and proportion of protein to liquor are very important in the effects on the leather produced. In fact it seems that the number of possibilities of operation and final results in chrome tanning is infinite.

Finishing Operations.—After the tanning operation is completed, the leather, if dried rapidly, is quite stiff, will usually break if bent sharply, and is not yet fit for use. The fibers must be lubricated to give them pliability and softness. Actually more work is required in the operations following the actual tannage than in all the preceding operations and processes put together. As each of the numerous kinds of leather requires a special series of operations, details will be impossible here.

If the tanned leather is not smooth, it is shaved by means of a machine with sharp blades. Very often it is split by means of a bandlike knife to obtain the desired thickness. (This may be done later, as shown in Fig. 1.) Vegetable-tanned leathers are sometimes washed, bleached, or scoured. The bleaching or washing is usually done in a revolving drum containing sodium carbonate, borax, or sulfuric acid. Other bleaching agents include sodium bisulfite, sulfurous acid, sulfite cellulose solutions, and various syntans.

The next operation involves the incorporation of oils and greases and is called *stuffing* or *fat liquoring.* The following classes of materials are used for this process: (1) true oils and fats, (2) soaps made from oils and fats, (3) sulfonation products of these oils and fats, (4) waxes, (5) resins, (6) hydrocarbons, (7) *moellon dégras* (oil from cod-liver oil), (8) egg yolk. The leather, either dry or wet, may be stuffed by hand or in a rotating drum. A more uniform job can be obtained by hand. Sometimes the leather is dipped into molten tallow, grease, or warm oil. Sole leathers are usually "loaded" with some material as magnesium sulfate and cellulose to give them desired properties.

The color and shade of the finished leather are produced by a combination of dyeing and finishing operations. Dyeing may be united with the fat-liquoring process, or it may be done before or after it. Most of the dyestuffs used at present are now synthetic coal-tar derivatives. The most common method of dyeing is in revolving drums or vats equipped with rotating paddles.

The finishing series of operations in the production of leather include both mechanical treatments and applications of finishing materials to the leather. The following classes represent the more common materials used in leather finishing: (1) proteins as egg whites, (2) gums and mucilages, (3) waxes, (4) resins, (5) dyes, (6) pigments, (7) lacquer materials, (8) antiseptics, (9) miscellaneous materials such as solvents, perfumes, soaps, sulfonated oils, metal salts, plasticizers, acids, and alkalies. Mechanical operations carried out in the finishing of leathers include staking (flexing the leather over an edge to loosen fibers and soften it), glazing, buffing, graining, trimming, rolling, brushing, and plating. The finishing operations alone embrace a technique requiring great skill, wide experience, and close attention.

Oil Tanning.[1]—From very early times skins have been tanned or preserved by the use of certain drying oils which have been worked into the skins and allowed to oxidize and react, thus becoming fixed. An example of this type of leather is that known as *chamois.* The sheep- or lambskins are subjected to the usual rinsing, liming, trimming, fleshing, and bating. They are then swollen preparatory to splitting, frequently with the aid of an acid such as sulfuric at a pH of around 2.0. The pickled skins in the plumped condition can be split easily, separating the grain from the flesh layer. The former is the skiver while the flesh layer is processed to make chamois leather. After this the depickling is carried out with an alkali such as borax or even soda ash or ordinary chalk with the pH around 7.0. The skins are now in condition to be processed with the oil to make chamois. The damp skins are treated with about 10 per cent of their weight of a suitable oil. The oils generally used are cod oil or linseed. Such oils as olive have no effect. This treatment with oil is often carried out in a drum where the revolving action extends over 4 hr. so that the oil can distribute itself and penetrate the skin. The skins are removed and piled in layers during which fermentation and oxidation proceed evolving a number of reactions that are not now well understood. The skins are hung or hooked for the reactions to proceed. The temperature rises some 20°F. during this maturing process. The oiling and hooking are repeated until 40 to 50 per cent of the oil on the weight of the moist skin has been incorporated. After the oil-tanning process is completed, the chamois leather is washed with warm alkalized water and hydraulically pressed to remove excess oil (*moellon dégras*). Further washing, buffing, and drying complete the operations.

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[1] Barrett, Manufacture of Chamois Leather, *Leather Trades' Rev.*, **75**, 1125–1130 (1942).

GELATINE

Gelatine[1] is an organic nitrogenous colloidal protein substance whose principal value depends on its coagulative, protective, and adhesive powers. Water containing only 1 per cent high-test gelatine by weight will form a jelly when cold. Glue and gelatine are closely related; indeed, glue may be looked upon as an impure gelatine. Both are derived by hydrolysis from collagen—the white fibers of the connective tissues of the animal body, particularly in the skin (corium), bones (ossein), and tendons. These reactions have been formulated.[2] However, these are only

$$\underset{\text{Collagen}}{C_{102}H_{149}N_{31}O_{38}} + \underset{\text{Water}}{H_2O} = \underset{\text{Gelatine}}{C_{102}H_{151}N_{31}O_{39}}$$

$$\underset{\text{Gelatine}}{C_{102}H_{151}N_{31}O_{39}} + \underset{\text{Water}}{2H_2O} = \underset{\text{Semiglutin}}{C_{55}H_{85}N_{17}O_{22}} + \underset{\text{Hemicollin}}{C_{47}H_{70}N_{14}O_{19}}$$

indications of the complex changes that take place, proceding from quite variable raw materials to almost as variable products.

Uses and Economics.—The industry recognizes three different kinds of gelatine: (1) edible, (2) photographic, and (3) inedible. In 1938, the United States production of edible gelatine was 23,132,000 lb., while the production of inedible and photographic gelatine was only approximately 7,000,000 lb.[3] Gelatine has recently become a widely consumed food. It is a very popular dessert which is easily assimilated and even helps in the digestion of other foods by forming an emulsion with fats and proteins. Gelatine is also quite widely added to ice creams to make the product smoother and to retard the crystallization of sugar when the ice cream is stored. Gelatine is also used by pharmaceutical houses for making capsules and as an emulsifier.

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[1] The spelling gelatine is adopted here because of its very wide usage in the industry although it is recognized that the spelling gelatin is used by *Chemical Abstracts* and the *U.S. Pharmacopoeia*.

[2] ALEXANDER, in "Rogers' Manual of Industrial Chemistry," 6th ed., p. 1588, D. Van Nostrand Company, Inc., New York, 1942.

[3] "Glues, Gelatines and Related Products," *U.S. Tariff Comm. Rept.* 135, 1940.

Gelatine has played an important part in the rapid development of the motion-picture and photographic industries. The gelatine is coated on the film base as the sensitized emulsion of the light-sensitive silver salts. Inedible gelatine is quite an arbitrary name and is applied to small amounts of gelatine used for miscellaneous purposes such as for sizing paper, textiles, and straw hats.

The prices of the different gelatines vary considerably. The average price of photographic gelatine is about 65 cents per pound while the average price of edible gelatine is only about half this figure. The tariff commission report lists producers of gelatine in the United States. It should be noted that a distinction is to be made between producers of gelatine and processors. The producer manufactures the plain clear gelatine which he sells to the processor who makes it up into gelatine dessert powders and other products. In 1939 imports of edible gelatine were about 10 per cent of the domestic consumption. Formerly, almost all of our photographic gelatine was imported, Germany being our chief source. Since the Second World War, however, the imports of this product are almost negligible.

Manufacture.—All three types of gelatine produced are made from calfskin, pigskin, or animal bones. These materials contain approximately one third collagen by weight. A large amount of the bones is imported chiefly from Belgium, while most of the pig- and calfskins are domestically produced. Approximately 50 per cent of the raw materials consumed are calfskin, 35 per cent pigskin, and 15 per cent bones. Although producers do not agree on which raw material yields the greatest quantity of gelatine, it is known that only the best grade raw materials, such as calfskins, are used for the production of photographic gelatine. Sheppard found that the presence of traces of mustard oil (allyl isothiocyanate) in gelatine prepared from the skins of calves that had eaten wild carrots was very effective in increasing photographic sensitivity.[1] The skins used for gelatine are usually imperfect ones, not suitable for making leather. It should be noted that strict government regulations and inspections govern the choice of raw materials used for the preparation of edible gelatine.

The bones and skins frequently undergo a *pretreatment* which makes the gelatine preparation easier. They are usually heated in lime and water to a temperature of about 70°C. for a short time. If higher temperatures and long heating are used, the gelatine hydrolyzes and loses part of its jellying properties.

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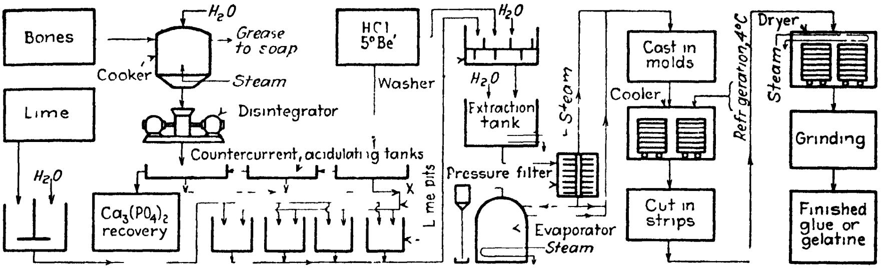
[1] SHEPPARD, Photographic Gelatine, *Phot. J.*, **65**, 380 (1925).

When bones are used as a raw material, they should be *degreased.* This is done by heating the bones under steam pressure and then running off the grease layer. Figure 2 shows the essential steps in the preparation of gelatine from bones. The bones are then crushed and enter a battery of four or more wooden tanks in series. Cold 5°Bé. (7.15 per cent) hydrochloric acid is passed countercurrent to the bones so as to flow into the most nearly exhausted ones first. The calcium phosphate, carbonate, and other mineral matter of the bones are dissolved, leaving the organic matter, collagen, with the residue from the bones. This is now called *ossein.* It is unnecessary to treat skins used in the manufacture of gelatine with hydrochloric acid because the collagen of skins is not shielded by mineral matter such as the calcium salts.



Note - Manufacture of glue and gelatine differs largely in that poorer grades of raw materials and higher extracting temperatures are used for the former Glue is more completely hydrolyzed than gelatine Instead of bones, skins, hides, sinews, hide scraps, fleshings, fish stock, etc, may be used, in which case, after washing, they are introduced at X Usually three extractions at temperatures from 60 to 75 deg C are used The last extract requires concentration before molding

Bones	3 03 tons	Steam	400 lb	To produce Gelatine, 1 ton $Ca_3(PO_4)_2$ 1 67 ton Grease, 0 08ton
Hydrochloric acid	1 14 tons	Electricity	55 kw-hr	
Lime	0 76 tons	Direct labor	6 man hr	

FIG. 2.—Flow sheet for glue and gelatine.

The ossein is soaked in concrete vats containing milk of lime for a period of a month or more. This same treatment is also given to hides used for gelatine production. The purpose of this soaking is for *plumping* and to remove and eliminate soluble proteins (mucin, albumin).[1] When the soaking in the lime is complete, the ossein or hides are washed in a rotary drum or conical-shaped washer, once with water, once with very dilute hydrochloric acid, and twice with water.

The next step in the preparation of gelatine is *extraction,* which is usually performed in wooden tanks equipped with steam coils. The extraction is made with water kept at 60 to 65°C. by the steam coils. The pH of the hydrolyzing liquid is of importance. The optimum range is 3.0 to 4.0.[2] The water is in contact with the ossein for approximately 8 hr. An 8 to 10 per cent solution of gelatine is obtained which is filtered hot and cooled. Then another warm extraction is made. The filtered liquors are run into long steel trays 6 in. wide and 6 in. deep, which are placed in refrigerated rooms to jell the contents. A third extraction of the ossein or hides is carried out at about 75°C. This is darker in color and so dilute that it will not set or jell on cooling. It is, therefore, necessary to evaporate this liquor under vacuum before it is cooled.

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[1] LEWIS, *et al., op. cit.;* PEARSON and SMITH, Gelatine, *Food Manuf.* **2,** 232, 287; **3,** 427 (1928).

[2] TUPHOLM, The Importance of pH Control in the Manufacture of Gelatine and Glue, *Food Manuf.,* **13,** 46 (1938).

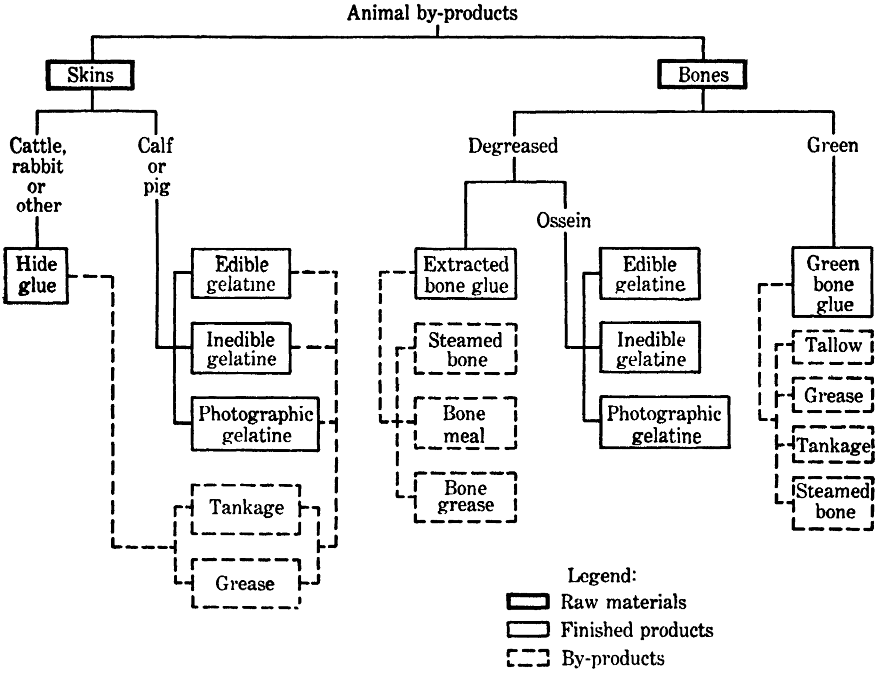

FIG. 3.—Animal glues and gelatines. (*After U.S. Tariff Commission Report* 135, 1940.)

Very often peroxides of hydrogen or sulfurous acid are used as a bleaching agent.[1]

The cooled solid gelatine is removed from the mold, cut into slabs ½ in. by 2 in. by 6 ft. These slabs are spread on nets which are stacked on small mobile trucks and pushed into a drying tunnel through which filtered air at about 40°C. is pulled by exhauster fans. On drying, the slabs shrink to a thin strip which may be ground to a powder for further usage.

Although gelatine itself is a by-product of the packing and tanning industries, its manufacture produces several more by-products, as shown in Fig. 3. By-products of gelatine made from pigskin or calfskin are tankage and grease. Gelatine made from degreased bones gives by-products of calcium phosphate for the pottery industry (bone china) and suitable as a fertilizer, and also bone black which is a good decolorizing agent.

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[1] RADLEY, Clarification and Bleaching of Gelatine and Glue, *Food Manuf.*, **11**, 242 (1936).

The production of edible gelatine must meet the requirements of the Food and Drug Administration, and the manufacture of photographic gelatine must undergo very rigid and specialized technical control. The process of making photographic gelatine is much more complicated than that used for producing other gelatines. It is for this reason that the price of photographic gelatine is nearly twice that of the edible variety. The reagents used must be very pure. For example, lime used in the process must be free from Fe and Mg salts, or else the gelatine cannot be used in photography.[1]

GLUES AND ADHESIVES

Though glues are often considered as insignificant materials, they are indispensable and necessary in the production of many of the commonly accepted necessities of life. Strictly interpreted, glue is derived from connective tissues of animals. However, many adhesives, not glues, are commonly called *glues* where they are used as substitutes for glue.

Historical.—Animal glue is the oldest type of glue, having been known for the past 3,000 years. It has been an important article of commerce for more than a century, while commercial production of other "glues" is chiefly a recent development. Casein adhesive and vegetable adhesive from starch became of commercial importance about a generation ago, soybean protein adhesive in the last decade; and synthetic resin adhesive has been developed only within the last few years.

Animal Glues.—These glues are made chiefly from waste products of the meat-packing and tanning industries such as fleshings, bones, trimmings, and materials unsuitable for the manufacture of gelatine, since the raw materials for the glue need not be selected with so great care as for gelatine. In 1935, approximately 575,000,000 lb. of such waste materials were consumed in the manufacture of animal glue.

Vegetable Adhesives.—Vegetable adhesives or glues were first found in large-scale industrial application approximately 30 years ago. The chief kinds of vegetable adhesives on the market of today are made from corn starch, tapioca flour, soybean protein, cassava starch, and potato starch. Vegetable adhesives may be applied cold and do not have the undesirable characteristic odors of some animal glues. This is one of the chief advantages of vegetable adhesives over animal glues, although most of them have the disadvantage of less strength than animal glues.

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[1] CHARRIOU and VALETTE, Manufacture of Photographic Gelatine, 15*me*. *Congr. chim. ind.*, 50 (1936); SHEPPARD, *op. cit.*

Economics and Uses.—Hide glue finds its greatest sales outlet to companies manufacturing furniture, abrasive paper and cloth, matches, automobiles, and printers' rollers. Extracted bone glue finds its chief outlet in the paper and paper product industries and to veneer manufacturers. The gummed tape and paper industry is the largest consumer of extracted bone glues. Other uses of animal glues include rug and carpet sizing, sizing straw hats, imitation leather, and the manufacture of insulation and materials from ground cork. In 1939, 63,983,949 lb. of hide and extracted bone glue, valued at $8,128,615, were produced in the United States.[1] Starch adhesives are widely applied for the manufacture of paper boxes and for labeling and sealing boxes, cans, and bottles. Tapioca adhesive is important in the manufacture of plywood and tapioca dextrin as an adhesive on envelopes. It is estimated that the U.S. Bureau of Engraving and Printing uses between 800,000 and 900,000 lb. of tapioca dextrin annually on postage stamps. Soybean protein adhesives first became of importance during the middle 1920's. Because of its strength, working qualities, cheapness, and physical characteristics such as being water-resistant, it has found widespread usage, especially in the making of plywood.

The value of the production of the three groups of commodities in 1939, embracing glues, gelatines, and allied products (*e.g.*, pectin and agar-agar) is estimated at nearly $35,000,000. Of this amount, approximately 60 per cent is for glue. It should be remembered that animal glues are by-products of other industries and not primary products.

MANUFACTURE

Animal Glues.—The manufacture of glue is almost identical with the manufacture of gelatine. The procedures include grinding bones, cutting hides and scraps into small pieces, degreasing the material by percolating a grease solvent through it, liming and plumping, washing, making several extractions by hot water, filtering liquors, evaporating, chilling, and drying the jelly slabs in a tunnel. When dry, the slabs of glue are flaked or ground, blended, graded, and barreled or bagged for shipment (see Figs. 2 and 3).

Variations of this process have been developed which do away with the tunnel drying and considerable hand labor. These consist of forcing the evaporated chilled extraction liquors containing 50 per cent glue through a wire grill or colander instead of placing slabs in a tunnel drier. The glue when forced through the wire grill is cut off into small pellets by knifelike blades. The pellets are dried in a three-stage drying system using bins and rakes to stir the pellets. In some processes the pellets are dropped from the colander or grill into a chilling bath, such as benzene, where they solidify. The adhering benzene evaporates and the pellets are dried. This pellet form of glue is known as *pearl* glue. However. more than three fourths of the glue produced in the United States is sold in the ground form and the remaining fourth is sold in the flake and pellet form, most of which is mainly flake.

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[1] "Manufactures, 1939, Miscellaneous Chemical Products," 16th Census of the United States, U.S. Department of Commerce, 1941.

Vegetable Adhesives.—The first vegetable glue on record was patented in 1874 and was prepared by the action of 8 per cent caustic soda on a suspension of potato starch in water. The mixture was heated until the starch granules burst. This treatment produced a highly adhesive mass and was recommended for use in the woodworking industry. Many modifications of this original process have been patented, but they all involve the same basic principle, *i.e.*, the modification of a starch solution with alkali. The most common starch used at present is cassava.

Other vegetable adhesives are prepared by treating various starches with cold alkalies, enzymes, and oxidizing agents. These are all wet processes, *i.e.*, a suspension of the starch in water is used. A wide variety of properties of the finished adhesive may be obtained by the proper selection of starch and gelatinizing agent.[1]

The manufacture of another type of vegetable adhesive or "glue" consists of taking a dry starch, such as tapioca or corn, and converting it into dextrin by means of a dilute acid and heat. To form the adhesive,[2] the dextrins are mixed with water and other ingredients by either the producer or the consumer. The soybean adhesive is made from soybean cake meal which has had its oil removed either by pressure or solvent extraction. The cake is ground to a fine flour, mixed with other ingredients, and sold.

Other Adhesives.—In 1938, the production of casein adhesive totaled more than 7,000,000 lb. It is a water-resistant, cold-working adhesive made from casein, which is a protein derived from milk. Casein is precipitated from skim milk by the addition of acid or by lactic acid developed on natural souring (see Chap. XXXIX). Approximately 4,000,000 lb. of fish glue are manufactured in the United States annually, having a value of approximately 20 cents per pound. It is a liquid glue made from waste materials of cod, haddock, cusk, hake, and pollock in a manner similar to animal glues. There are many more adhesives on the market, such as sodium silicate solutions, mucilage which is a solution of gum arabic or acacia in water, latex-type rubber adhesives, cellulose ester adhesives, phenol formaldehyde resins, chlorinated rubber, and chloroprene adhesives.[1]

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[1] WALTON, "A Comprehensive Survey of Starch Chemistry," vol. 1, Chap. 15, Reinhold Publishing Corporation, New York, 1928.

[2] LEWIS, *et al.*, *op. cit.*

Table 7.—Hide and Bone Glue[a]

Year	Production	*Quantity, thousands of pounds*		
		Sales	Imports	Exports
1935	56,686	64,812	2,261	986
1936	70,347	73,371	5,686	1,197
1937	74,145	65,754	4,102	1,121
1938	51,435	51,101	1,003	966

[a] Glues, Gelatines and Related Products, *U.S. Tariff Comm. Rept.* 135, 1940.

Table 8.—Vegetable Glues[a]

Year	Quantity, lb.	Production value	Value per lb.
1935	126,792,581	$5,204,473	$0.041
1937	229,995,918	8,621,874	0.037
1938	165,645,012	8,115,842	0.049

[a] Glues, Gelatines and Related Products, *U.S. Tariff Comm. Rept.* 135, 1940.

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[1] Bigelow, Adhesives Industry Is Modernized, *Chem. & Met. Eng.*, **49,** 121 (1942); Perkins, Industrial Adhesives, *Product Eng.*, **10,** 135 (1939).

CHAPTER XXVI

PESTICIDES

This chapter covers the use of chemicals to control either plant or animal life disadvantageous to man and his domestic animals. Reliable authorities have estimated[1] the damage caused by insects in the United States to be at least 2 billion dollars annually, while injurious fungi cause a loss of about 1 billion dollars a year. The weed and plant pests rob farmers of 3 billion dollars[2] annually. It cannot be stated too strongly that this large loss would be still larger were not these pests kept under some measure of control by the use of chemicals, accompanied by other means, such as the proper cultivation of the soil and the appropriate construction of homes and barns.

Every citizen is concerned with this tremendous loss and should be interested in the chemical warfare directed against man's normal enemies. It is a most important step in the conservation of our resources and in increasing the productivity of our soil. The chemical engineer is called upon to manufacture these domestic chemical warfare agents and in special conditions to assist in their application. This chapter will present, in general, the use of these compounds and, in particular, the means for the manufacture of products for pest control, whether the pests be plants or animals, macro or micro in size, or whether the pests be disturbing our food, our bodies, our clothing, or our habitations.

Very considerable sums are spent for the chemical agents to control these depredations, the retail sales being roughly $200,000,000 annually. A few of our principal pesticides were produced or imported during 1939 in the following quantities:

INSECTICIDES AND FUNGICIDES

Lead arsenate	59,568,596 lb.
Calcium arsenate	39,281,788 lb.
Lime-sulfur solution	9,491,068 gal.
Pyrethrum flowers (1940 imports)	12,591,220 lb.
Rotenone-bearing roots (1940 imports)	6,556,815 lb.

INSECTICIDES

Insecticides are agents or preparations for destroying insects and are usually classified according to their method of action. *Stomach poisons*

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[1] ROARK, Insecticides, Fungicides and Hormone Sprays, *Ind. Eng. Chem.*, **34**, 489 (1942).

[2] TAYLOR, Chemical War on Weeds, *Country Gentleman*, February, 1942.

are lethal only to insects that ingest them; contact insecticides kill following external bodily contact; and *fumigants* act on the insect through the respiratory system. Table 1 lists the principal insecticides in each class. They may be applied as a spray if liquid or in solution, as a dust, or as a gas.

TABLE 1.—INSECTICIDES CLASSIFIED ACCORDING TO METHOD OF ACTION

Stomach poisons	Contact insecticides	Fumigants
Paris green	Sulfur	Sulfur dioxide
Lead arsenate	Lime-sulfur	Nicotine
Calcium arsenate	Nicotine sulfate	Hydrocyanic acid
Sodium fluoride	Pyrethrum	Naphthalene
Cryolite	Rotenone	*p*-Dichloro-benzene
Rotenone	D.D.T.	Ethylene oxide

History.—Records show that insecticides were used as long ago as 1000 B.C. However, they were more often useless than useful as they were based on legend and superstition rather than on scientific knowledge. The essential property of early insecticides was a disagreeable odor rather than a poisonous nature. Although the toxic properties of arsenic were known as early as A.D. 40, it was not employed in the western world until 1669. About the middle of the last century the use of paris green, lead arsenate, and other really poisonous chemicals was started as a general method of insect control.[1]

Inorganic Insecticides.—Inorganic compounds are widely used as insecticides. They are very effective, but extreme precautions should be taken to prevent poisoning of the men handling them. Fruits should be washed in order to obviate hazard to the consumer.

Paris green is a double salt of copper arsenite and copper acetate, $Cu(OOCCH_3)_2 \cdot 3Cu(AsO_2)_2$. It may be prepared by treating copper arsenite with dilute acetic acid. The *unit processes* (Pr.) and *unit operations* (Op.) in the manufacture are as follows:[2]

Finely powdered arsenic trioxide (white arsenic) is dissolved in a 45 per cent soda-ash solution at 70 to 80°C. in a large tub equipped with steam coils and a stirrer (Pr.).

A solution (approximately 27 per cent) of copper sulfate is prepared, heated to 90°C., and added to the soda-ash-arsenic solution. The mixture is stirred to aid the evolution of carbon dioxide. The copper arsenite precipitates (Op. and Pr.).

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[1] SHEPARD, "The Chemistry and Toxicology of Insecticides," Chap. II, Burgess Publishing Co., Minneapolis, 1939.

[2] ULLMANN, "Enzyklopaedie der technischen Chemie," 2d ed., vol. 1, p. 588, Urban and Schwarzenberg, Berlin and Vienna, 1928–1932.

When a thick layer of copper arsenite has collected on the bottom of the vat, the acetic acid is added. This should be quite dilute (10 to 12 per cent) in order to prevent too vigorous an evolution of carbon dioxide. The temperature is maintained at 82 to 85°C. (Pr.).

The mixture is allowed to stand for 2 to 3 hr. until no more gas is evolved and the formation of the paris green is complete (Pr.).

The precipitate is washed with hot water (Op.), filtered through a press (Op.), broken into small pieces (Op.), and dried at 35°C. (Op.).

Commercial paris green contains the equivalent of 54 to 57 per cent arsenic trioxide. It is not used so widely as some of the other arsenicals because of its burning effect on the foliage of plants. Its chief use is in controlling the potato beetle and in covering water to control malaria-carrying anopheline mosquito larvae.[1]

The *lead arsenate* commonly used as an insecticide is an acid lead arsenate, $PbHAsO_4$. Many other lead arsenates, $Pb_2As_2O_7$, $PbH_2As_2O_7$, etc., are known and occasionally employed for this purpose. Acid lead arsenate may be prepared by the following series of reactions:[2]

$$3PbO + 2CH_3CO_2H \rightarrow (CH_3CO_2)_2Pb\cdot 2PbO + H_2O$$
$$(CH_3CO_2)_2Pb\cdot 2PbO + 2H_3AsO_4 \rightarrow Pb_3(AsO_4)_2 + 2CH_3CO_2H + 2H_2O$$
$$Pb_3(AsO_4)_2 + 2HNO_3 \rightarrow 2PbHAsO_4 + Pb(NO_3)_2$$
$$Pb(NO_3)_2 + H_3AsO_4 \rightarrow PbHAsO_4 + 2HNO_3$$

The actual manufacture of acid lead arsenate is much simpler than the equations indicate. Litharge is dissolved in the calculated quantities of acetic acid and nitric acid. The theoretical quantity of arsenic acid is added, the precipitated lead arsenate removed by filtration, and the mixture of acetic and nitric acids in the filtrate used over again. Three precipitations of lead arsenate can be made before the spent acid has to be strengthened or discarded. The yields range from 95 to 97 per cent. Lead arsenate may also be prepared in colloidal form by precipitation in the presence of gelatine which acts as a protective colloid.[3]

About 30,000 tons of lead arsenate were consumed in the United States in 1939. It is the most widely used of the arsenical insecticides, especially for the control of the codling moth in apple orchards and against the potato beetle. The commercial product contains the equivalent of 31 to 33 per cent arsenic trioxide. All white arsenicals are now colored pink to safeguard against confusion with foods such as flour and baking powder.

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[1] SHEPARD, *op. cit.*, Chap. V.

[2] ALLEN, U.S. Pat., 1427940 (1922).

[3] BRINLEY, Preparation and Properties of Colloidal Arsenate of Lead, *J. Agr. Research*, **26**, 373 (1923).

Calcium arsenate is cheaper than lead arsenate but does not adhere so well to leaves, thus rendering it less effective. Three calcium arsenates are known, $CaH_4(AsO_4)_2$, $CaHAsO_4$, and $Ca_3(AsO_4)_2$. Both the monocalcium arsenate and dicalcium arsenate are too soluble in water to be used as insecticides. The commercial insecticidal product is usually a mixture of tricalcium arsenate, $Ca_3(AsO_4)_2$, and lime, called *basic* calcium arsenate. The manufacture of basic calcium arsenate may be carried out by adding a dilute solution of arsenic acid to a saturated solution of hydrated lime.[1] To prevent the formation of crystals of soluble dicalcium arsenate coated with insoluble tricalcium arsenate, the arsenic acid solution is atomized into the lime solution and the mixture vigorously agitated. The chief use of calcium arsenate is to control the cotton boll weevil, although it is often used instead of lead arsenate for codling moth control.

Fluorine compounds are promising stomach-poison insecticides as substitutes for the arsenicals. As they are also extremely poisonous to man, caution should be observed in their application and handling. Fluorine compounds are obtained as a by-product from rock phosphate treatment, thus assuring an economical source.

The fluorides are too water-soluble to be used on plants, but sodium fluoride is widely used to control roaches and poultry lice. Some of the fluosilicates and fluoaluminates may be applied to crops because of their decreased solubility. The principal compounds that are suitable are barium fluosilicate and sodium fluoaluminate (cryolite). Cryolite is a natural mineral although synthetic cryolites are available. Its use as an insecticide is very minor compared to its consumption in the manufacture of aluminum (see Chap. XVI).

Sulfur and *sulfur compounds* are employed to some extent as contact insecticides, but their chief use is as fungicides. Sulfur dioxide often serves as a fumigant. The manufacture of sulfur has been discussed in Chap. XIX. Several forms of sulfur are applicable for insecticides—ground, flowers, conditioned, and wettable. Conditioned sulfur, often called *dusting* sulfur, is prepared by adding about 1 per cent of talc, gypsum, or clay to ground sulfur to render it free-flowing.[2] Wettable sulfur is any form of powdered sulfur to which a suitable wetting agent has been added.

Sulfur is generally employed as a dust and, therefore, uniformity and smallness of particle size are important.[3] Wettable sulfurs are designed for use, suspended in water, as a spray. As an insecticide, sulfur is applicable for the control of mites, spiders, and other insects of this type.

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[1] NELSON, Preparation of Calcium Arsenates of Low Solubility, *J. Econ. Entomol.*, **32**, 370 (1939).

[2] SHEPARD, *op. cit.*, Chap. VII.

[3] GOODEN, Commercial Insecticidal Sulfurs, *Ind. Eng. Chem.*, **33**, 1452 (1941).

A mixture of lime and sulfur (lime-sulfur), prepared by boiling milk of lime with sulfur, is useful as a spray to control scale insects.[1]

Sulfur dioxide is the oldest known fumigant. It is usually made *in situ* by burning candles of molded sulfur. Although it is injurious to living plants and so cannot be applied on trees, it is effective for the fumigation of homes and granaries.

Hydrocyanic acid is an efficient fumigant for many pests, especially insects. Large quantities are used in the citrus fruit industry and smaller amounts for greenhouse and household fumigation. When applied on a small scale, the gas is generated as needed by adding sulfuric acid to "eggs" of sodium cyanide. The citrus fruitgrowers, however, use a commercially manufactured liquid product that contains 97 per cent hydrocyanic acid.

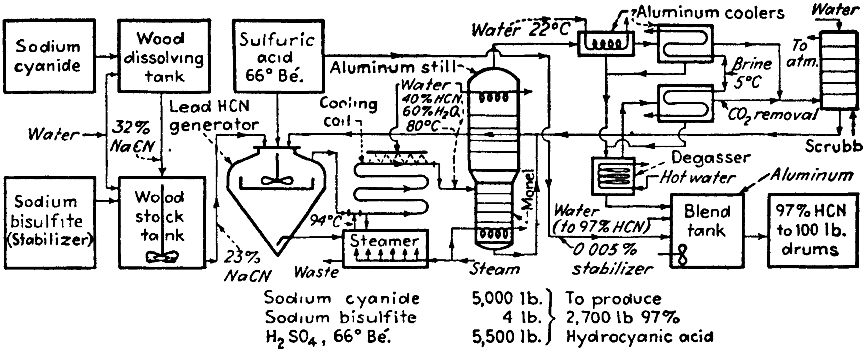

FIG. 1.—Manufacture of liquid hydrocyanic acid.

The steps in the manufacture[2] are as follows, as shown in Fig. 1. An aqueous solution of sodium cyanide (Chap. XIV) is mixed with concentrated sulfuric acid and allowed to react. Most of the hydrocyanic acid is expelled by the heat of the reaction. The remainder is removed by heating the residual solution of sodium sulfate with live steam to 103 to 104°C. The mixture of hydrocyanic acid and steam is passed through a cooler where some of the steam condenses and the vapors are sent to a still. Water, almost free of hydrocyanic acid, is collected at the bottom of the still and the vapor is fairly pure hydrocyanic acid. The vapors are conducted through two condensers. The first is cooled with water and about 30 per cent of the acid is liquefied. The second condenser is cooled with brine to liquefy the remainder of the acid. The liquid hydrocyanic acid is degassed to remove carbon dioxide impurity and is adjusted to standard concentration (97 per cent), stabilized with 0.005 per cent by weight of sulfuric acid, and packed into tinned steel drums.

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[1] DAVIS, "Insecticides and Their Uses," *Bull. Purdue Univ.*, Pharmacy Extension Series I, Purdue University, Lafayette, Ind., 1932.

[2] CARLISLE, The Manufacturing, Handling and Use of Hydrocyanic Acid, *Trans. Am. Inst. Chem. Engrs.*, **29**, 113 (1933).

To fumigate a citrus grove, each tree is covered with an airtight cotton tent. The liquid hydrocyanic acid is vaporized or sprayed inside the cover to produce an effective concentration. Care must be taken in handling this material as it is not only a powerful insecticide but also an extreme poison to men and animals.

Plant Derivatives.—Many of the plant derivatives used as insecticides depend for toxicity upon the alkaloids that they contain. The toxic principle of the plant often does not exhibit its poisonous effect until it is removed from the plant. Tobacco plants, for example, are often seriously injured by insects that are readily killed by nicotine extracts.[1]

Nicotine is a volatile alkaloid obtained by extracting ground waste tobacco leaves and stems with water. Because of its volatile nature, the nicotine is usually converted to the sulfate and sold as 40 per cent solution. Nicotine sulfate solution is widely used as a contact insecticide to control codling moths and aphids. It is generally combined with soap solution to enhance the spreading of the film on the plant and to liberate slowly the free nicotine which is the active killing agent. Nicotine-impregnated paper is often burned to fumigate greenhouses and poultry houses.

Pyrethrum.—Flowers of the pyrethrum plant (a type of chrysanthemum) contain toxic, nonnitrogenous organic esters (pyrethrins). The principal source of pyrethrum is Japan, although small quantities are grown in Yugoslavia, East Africa, and Brazil. The importance of this material as an insecticide is shown by the fact that the United States imported over 12,000,000 lb. in 1940 in the form of compressed bales of the flowers. The bales are broken up, ground to a fine powder, and extracted several times with a chlorinated hydrocarbon. (Carbon tetrachloride is often used.) The extract is concentrated by removing the solvent in a vacuum still below 60°C., and the resulting oleoresin is employed to prepare the finished insecticides.[2]

The oleoresin may be dissolved in a water-soluble organic solvent, such as alcohol or acetone, or emulsified with soap. These concentrated solutions are diluted with water and applied as garden sprays. The chief use of pyrethrum extract is as a fly, roach, and bedbug spray. For this purpose the oleoresin is dissolved in kerosene or mineral solvents.[3]

To further the activity of pyrethrum dissolved in kerosene for fly and other insect sprays, certain activators have been employed. For instance, it has been shown[1] that a naval stores product, ethylene glycol ether of pinene, known commercially as "D.H.S. Activator," accentuates the action of pyrethrum and also of rotenone. It has likewise been shown that certain substitutions can be made effectively for pyrethrum. Among such is a domestic product, fenchyl-thiocyanyl acetate, known commercially as Thanite.[2]

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[1] SHEPARD, *op. cit.*, Chap. IX.

[2] GNADINGER and CORL, Manufacture of Concentrated Pyrethrum Extract, *Ind. Eng. Chem.*, **24**, 988 (1932).

[3] SHEPARD, *op. cit.*, Chap. IX.

Rotenone[3] is the poisonous principle of the roots of several tropical and subtropical plants, chief among which is derris. It is a nonnitrogenous complex organic heterocyclic compound, $C_{23}H_{22}O_6$. The rotenone is obtained by extracting the ground derris roots with chloroform or carbon tetrachloride. Other compounds related to rotenone, but not so toxic, are also present in the extract. However, no attempt is usually made to separate the rotenone from these materials. The solvent is removed and the residue is dissolved in water-soluble solvents such as acetone.

Rotenoid compounds are effective stomach and contact poisons. They have long been used as fish poisons by natives of the East Indies and Japan, but their chief applications in the United States are as insecticides. Powdered derris root often serves as an insect powder.[4]

Red squill is prepared from the bulb of a subtropical lily plant that grows wild in southern Italy. The bulbs are dried and ground to a fine powder. It is extensively used as an ingredient of poison baits, especially for use against rats. Although lethal to rodents, it is not harmful to domestic animals or poultry and thus may be used when poison baits would not be practical.

Organic Chemicals (Other than from plants).—Most of the insecticides in the past have been either inorganic in nature or plant derivatives. The inorganic compounds are extremely toxic to man and present a considerable health hazard from the spray residues on fruits and vegetables. The plant derivatives are, in general, less toxic to man, but the difficulty of obtaining them from the various parts of the world, especially in wartimes, has rendered the search for synthetic substitutes imperative.

Naphthalene is one of the principal constituents of coal tar (Chap. VI). It has been used for many years as a repellent for clothes moths, although it is not usually employed in concentrations strong enough to be fully effective. An ordinary trunk requires about 2 lb. of naphthalene to protect the contents. It is also an efficient soil and greenhouse fumigant.

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[1] Mentzer, Daigh, and Connell, Agents for Increasing the Toxicity of Pyrethrum to Mosquito Larvae and Pupae, *J. Econ. Entomol.* **34,** No. 2, 182 (1941); Pierpont, Effect of a Terpene Ether on Certain Fly Sprays, *J. Econ. Entomol.*, **34,** No. 2, 195 (1941).

[2] U.S. Pats., 2209184 of July 23, 1940; and 2217611 of Oct. 8, 1940; secondary terpene alcohol derivatives.

[3] LaForge, Haller, and Smith, The Determination of the Structure of Rotenone, *Chem. Rev.*, **12,** 181 (1933).

[4] Roark, Rotenone, *Ind. Eng. Chem.*, **25,** 639 (1933).

o- and *p-dichloro-benzenes* are by-products in the making of monochloro-benzene and are available in large quantities at a reasonable cost. The paracompound is used as a fumigant for soils, clothes, and to a very limited extent for grains. The chief insecticidal application is to control the peach-tree borer. About 500,000 lb. a year are consumed in the Georgia peach belt for this purpose.[1] The orthocompound finds extensive use in termite control. It is generally forced under pressure into the wood to be treated and acts as a termite repellent.

D.D.T. or Dichloro-diphenyl-trichloro-ethane.—This old product, in the light of recent investigations, is proving of great value as a contact insecticide against lice on human beings and flies in general. It is made by treating chloral or chloral hydrate with chloro-benzene using 20 per cent oleum as a dehydration agent. Although the crude product can be used, a purer one can be obtained by recrystallization from alcohol when a product, melting at 108°C., is obtained.

Ethylene oxide is a low-boiling (11°C.) liquid that is produced by the catalytic oxidation of ethylene or by hydrolysis of ethylene chlorohydrin (Chap. XXXIX). Because of its great volatility it is particularly applicable as a fumigant for grain. For this purpose it is usually mixed with 9 parts of carbon dioxide to 1 part of ethylene oxide (Carboxide). This mixture is easily liquefied, is nonflammable, and does not produce an objectionable taste in the grain thus fumigated.

Chloropicrin, CCl_3NO_2, is better known as a war gas than as an insecticide. It is a colorless liquid that is readily volatile and is used as a fumigant for grains. It is toxic to plants and seeds as well as to insects and for this reason has been employed as a soil fumigant. For many years it has been prepared by the action of bleaching powder on picric acid. The recent commercial availability of nitro-methane affords a new source for this compound.

$$CH_3NO_2 + 3Cl_2 \rightarrow CCl_3NO_2 + 3HCl$$

Miscellaneous Organic Compounds.—Many compounds have been synthesized and tested for insecticidal activity. The U.S. Department of Agriculture has investigated about 2,000 since 1932.[2] Only a few of these will be mentioned.

Neonicotine, β-pyridyl-α-piperidine, is prepared by the reaction of sodium on pyridine. It is the racemic form of the naturally occurring, optically active anabasine (extracted from *Anabasis aphylla L.*). It is more toxic to aphids than nicotine but not so effective against other insects.[1]

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[1] SHEPARD, *op. cit.*, Chap. X.

[2] SMITH, Synthetic Organic Compounds as Potential Insecticides, *Ind. Eng. Chem.*, **34**, 499 (1942); HALLER, Search for New Insecticides, *J. Chem. Education*, **19**, 315 (1942), bibliography.

Phenothiazine, $C_{12}H_9NS$, is a heterocyclic compound that appears to be more toxic than rotenone to mosquito larvae and as effective as lead arsenate in codling moth control. It is available in large quantities at a reasonable cost.[2]

Other promising new insecticides are *o*-, *m*-, and *p*-iodonitro-benzenes, *p*-amino-acetanilide, *o*-, *m*-, and *p*-nitro-phenyl-iodochlorides, halogenated acetanilides, derivatives of dithiocarbamic acid, and derivatives of 1,3-indandiones.[3] Dinitro-anisol is also attracting some attention.

FUNGICIDES

Fungi belong to the plant kingdom and thus fungicides are agents for destroying lower forms of plant life rather than insects. Fungi are parasitic plants that are capable of destroying higher plants, thus robbing man of valuable foods or materials. They may attack seeds, the growing plant, or plant material such as wood. Fungicides act by direct contact and often injure the higher plant as well as the fungus. The production of a fungicide that is effective in destroying the fungi and not the host is a difficult problem.[4]

History.—The use of an effective fungicide was probably discovered by accident. It was common practice in the eighteenth and early nineteenth centuries to cover grapevines along the road with a poisonous white powder to discourage thievery. Copper sulfate and lime (Bordeaux mixture) were often used for this purpose but it was not until 1883 that it was noticed that this mixture controlled the downy mildew of the vines. Other substances, such as copper sulfate, were tried on a very small scale as fungicides in the early part of the nineteenth century, but they caused so much damage to the plants that their use did not become widespread.

Inorganic Fungicides.—The inorganic fungicides are usually salts of heavy metals such as copper, zinc, and mercury, although acid-forming materials such as sulfur may be used.

Bordeaux mixture is the most widely used fungicide in the United States. It is simple to make at home, although a commercial preparation is available. Several formulas are often given for its preparation, but the 4-6-50 formula is generally recommended.[1] Four pounds of copper sulfate is dissolved in one vessel and 6 lb. of hydrated lime mixed with water in another. Each is diluted to 25 gal. and poured simultaneously through a strainer into a third container. This mixture cannot be stored without losing its fungicidal activity. It is effective for control of most of the common molds and mildews. It cannot be used on peach trees as these leaves are injured by copper-containing sprays. However, most of the common vegetables and fruits can be safely treated with Bordeaux mixture.

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[1] Roark, Insecticides and Fungicides, *Ind. Eng. Chem.*, **27**, 530 (1935).

[2] Smith, *op. cit.*

[3] Tisdale and Flenner, Derivatives of Dithiocarbamic Acid as Pesticides, *Ind. Eng. Chem.*, **34**, 501 (1942); Kilgore, Ford, and Wolfe, Insecticidal Properties of 1,3-Indandiones, *Ind. Eng. Chem.*, **34**, 494 (1942).

[4] Sessions, Fungicide Adjustment to Meet Requirements of Disease and Host, *Ind. Eng. Chem.*, **28**, 287 (1936).

Zinc Chloride–Sodium Dichromate.—An aqueous solution of zinc chloride containing 20 to 25 per cent of sodium dichromate is widely consumed as a wood preservative. Most fungicides owe their effectiveness to their ability to destroy the fungus spores. This mixture, however, proves just as effective, but its action is brought about by rendering the host material toxic to the fungus. It cannot be used on living plants. The solution is forced into the wood under pressure at a temperature below 110°F. The wood so treated is very resistant to rotting (caused by fungus growth which digests and thus destroys the wood).[2] A great advantage of this type of wood treatment is that the appearance is unchanged and paint may be applied.

Mercury Chlorides.—Both mercurous and mercuric chlorides are effective fungicides. Mercurous chloride (Hg_2Cl_2, calomel) is prepared by heating 4 parts of mercuric chloride with 3 parts of metallic mercury in an iron pot until a white mass is formed. The temperature is raised to sublime off the mercurous chloride which is further purified by washing. Mercuric chloride ($HgCl_2$, corrosive sublimate, bichloride of mercury) is manufactured by heating mercury in the presence of chlorine gas or by heating equal parts of mercuric sulfate with common salt.

A mixture of these two chlorides, Calo-clor, is used as a turf fungicide to control brown patches. It is applied by spray as a water suspension. Either the mercurous or mercuric compound may be used for fungicidal treatment of seeds. In general, these compounds are too injurious to plants to be applied similarly to Bordeaux mixture.

Organic Fungicides.—The organic fungicides are widely varying in composition. As yet, there does not seem to be any well-defined relationship between structure and fungicidal activity.

Formaldehyde is prepared by the oxidation of methanol (Chap. XXXIX) and is sold as a 40 per cent solution in water, called *Formalin*. It serves to control smut, scab, and rot fungi of common garden vegetables very effectively. Care should be taken not to apply too great a quantity because in higher concentrations it is harmful to the host plants. Seed-borne fungus diseases are often controlled by soaking the seeds in highly diluted formaldehyde before planting.

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[1] DAVIS, "Insecticides and Their Uses," *Bull. Purdue Univ.*, Pharmacy Extension Series I, Purdue University, Lafayette, Ind., 1932.

[2] DAVIS, Lengthening the Life of Wood, *Chem. Markets*, **30**, 257 (1932); THIESSEN, Chemical Preservation of Wood, *Chem. Markets*, **32**, 323 (1933).

Creosote.—Coal-tar creosote (Chap. VI) has long been the standard substance to be used for wood preservation. It is effective, permanent, and inexpensive, but it has a penetrating odor. Because of the dark stain it imparts, wood so treated cannot be painted. However, for many purposes, such as treating fence posts, railroad ties, etc., these disadvantages are not of importance. Recently, bleached and deodorized creosote has been made available.

Mercurials.—Several organic mercurials are effective fungicides. The important ones in use are ethyl-mercuric chloride, pyridyl-mercuric salts, ethyl-mercuric phosphate, hydroxy-mercurichloro-phenol, and phenyl-mercuric salts.

Ethyl-mercuric chloride may be prepared by treating tetraethyl lead with mercuric chloride.

$$Pb(C_2H_5)_4 + 4HgCl_2 \rightarrow 4C_2H_5HgCl + PbCl_2 + Cl_2$$

These compounds are sold as dusts or solutions under various trade names (Semesan, Ceresan, etc.) and are used to treat seeds, to prevent the formation of lumber sap stain, and as general garden sprays.[1]

3-Pyridylmercuric Salts.—Recent developments of interest in the field of mercurial fungicides and antiseptics center about the 3-pyridylmercuric salts.[2] Pyridylmercuric chloride, pyridylmercuric acetate, and pyridyl-mercuric stearate form a versatile group of effective fungicides, said to be equal or superior to the analogous phenylmercuric salts in bactericidal and fungicidal activity and less irritating to the skin.

Pyridylmercuric chloride is reported[3] to be effective against *Staphylococcus aureus* in dilutions of 1:550,000 to 1:1,200,000. In *in vivo* studies[4] it has been shown to compare favorably with other mercurial antiseptics, which, as a group, were superior to commonly used antiseptics such as tincture of iodine. Pyridylmercuric acetate has been found to be outstandingly effective in fungusproofing the surface of cork and wool-felt gasket and sheet. The stearate, because of its solubility in organic solvents, is well adapted to incorporation in paints and lacquers. When the stearate is applied to fibrous materials, it imparts water repellency along with the antifungal property. The chloride, although of only limited solubility, can also be used in paints and lacquers. It is applied to textiles by first impregnating the cloth with a solution of pyridyl-mercuric hydroxide made by dissolving the chloride in an alkali solution and subsequently reprecipitating the chloride in the fibers by acidification. Textiles so treated show a high degree of retention of the fungicide in weathering and leaching tests.

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[1] TISDALE, Ethyl Mercury Compounds as Agricultural Disinfectants, *Ind. Eng. Chem.*, **24**, 745 (1932); "Vegetable Seed Treatments," *U.S. Dept. Agr. Farmers' Bull.* 1862, 1942; "Cottonseed Treatments," *U.S. Dept. Agr. Leaflet* 198, 1940; "Disinfecting Seed Potatoes," *U.S. Dept. Agr., Misc. Pub.* 53, 1929; "Treat Seed Grain," *U.S. Dept. Agr. Misc. Pub.* 219, 1937.

[2] Mallinckrodt Chemical Works, St. Louis, Mo.; SHREVE, *et al.*, U.S. Pats. 2206309 (July 2, 1940), 2216140 (Oct. 11, 1940), 2297639 (Sept. 29, 1942).

[3] SWANEY, SKEETERS, and SHREVE, *Ind. Eng. Chem.*, **32**, 360 (1940).

[4] VASS, *J. Pharmacol.*, **66**, 279 (1939).

HERBICIDES

Weeds rob the American farmer of about 3 billion dollars each year. The chemical control of these pests is a comparatively new development. It involves a difficult problem, that of killing the objectionable plants and not injuring the desirable ones.

The older types of herbicides were actually soil sterilants; they killed all plant life for a period of at least 3 years. Sodium chlorate (Chap. XVI), sodium arsenate, borax (Chap. XIV), and chloropicrin have been widely used as soil sterilants. Recently selective herbicides which are capable of killing broad-leaf plants but leave grains and grasses unaffected have been introduced. One of the most effective of these selective herbicides is a 10 per cent solution of sulfuric acid. Applied to wheat, oat, or barley fields it has been found to increase the yields as much as 60 per cent.

A very promising substance among the new selective herbicides is 4,6-dinitro-*o*-cresol (Sinox).[1] It may be applied to all grass and grain crops and produces only a mild yellowing of the valuable crop. The objectionable weeds are almost entirely eliminated by this treatment. A new inorganic herbicide of much promise is sulfamic[2] acid, $HO{\cdot}SO_2{\cdot}NH_2$, which is now being given extensive tests. It seems to be particularly effective against poison ivy.

GERMICIDES, ANTISEPTICS, DISINFECTANTS

A germicide is anything that destroys germs (pathogenic microorganisms); an antiseptic is a substance that prevents or arrests the growth or action of microorganisms; a disinfectant is an agent that frees from infection.[3] These terms are often used interchangeably. Strictly speaking, the use of *antiseptic* should be restricted to living tissue and *disinfectant* to inanimate objects. The effectiveness of these types of materials is usually expressed in terms of the *phenol coefficient*. The killing power of pure phenol on pure cultures of *Eberthella typhosa* and

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[1] TAYLOR, *op. cit.*

[2] CUPERY and GORDON, Sulfamic Acid, *Ind. Eng. Chem.*, **34**, 792 (1942).

[3] PATTERSON, Meaning of "Antiseptic," "Disinfectant" and Related Words, *Am. J. Pub. Health*, **22**, 465 (1932).

Staphylococcus aureus is arbitrarily set as unity, and the unknown material is rated in comparison. Table 2 lists the phenol coefficients of some of the common germicides, antiseptics, and disinfectants.

TABLE 2.—PHENOL COEFFICIENTS[a]

Compound	*Staphylococcus aureus*	*Eberthella typhosa*
Phenol	1	1
Chloramine	133	100
Dakin's solution	......	0.78
Lysol	3.2	5.0
Hexylresorcinol	150	72
Mercurochrome	1.7	
Merthiolate	40–50	40–50
Metaphen	1500	
Tincture of iodine, U.S.P.	38	

[a] LANGE, "Handbook of Chemistry," 4th ed., p. 1495, Handbook Publishers, Inc., Sandusky, Ohio, 1941.

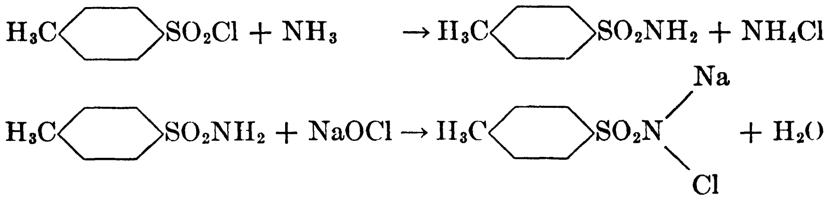
The use of germicides began with the discovery of the effectiveness of phenol (carbolic acid) by Lister in 1867. While efficient, it caused serious injury to body tissues when applied in too strong concentrations. It also was a powerful poison to man. Consequently the less toxic germicides are being favored. Most of the important germicides are organic compounds, the well-known tincture of iodine being the chief exception. The common germicides and antiseptics may be classified as nonmetallic and metallic compounds.

Nonmetallic Compounds.—Nonmetallic germicides can be highly efficient (see Table 2). They differ widely in chemical structure and only a few of the extensively used compounds will be discussed. The literature on chemicals suggested for this purpose is voluminous.

Tincture of Iodine.—Tincture (meaning alcoholic solution) of iodine (Chap. XXI) has been the standard household germicide. Recently, more effective compounds have been made available that eliminate some of the disadvantages of this solution. Unless the containers are kept tightly capped, part of the alcohol evaporates leaving a more concentrated iodine solution from which serious burns have resulted.

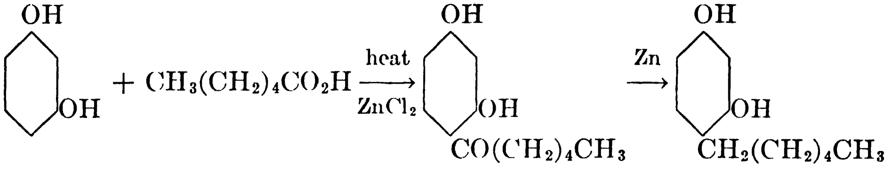
Phenol and *cresols* (Chap. VI and XXXVIII) are effective germicides. Care should be taken in the use of phenol because of its caustic nature. Cresols (especially *m*-cresol) are not soluble in water and are usually sold in the form of emulsions (Lysol, for example). The emulsions are less caustic and less toxic than phenol.

Dakin's Solution and Chloramine.—Dakin's solution is a 0.45 per cent solution of sodium hypochlorite prepared by the action of chlorine on sodium carbonate. It is effective as a surgical germicide and was used extensively in The First World War. Chloramine (chloramine T, Chlorazene) is sodium *p*-toluene-chlorosulfonamide. It is prepared from *p*-toluenesulfonyl chloride which is available in quantity as a by-product in the making of saccharin.[1]

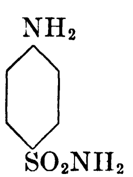


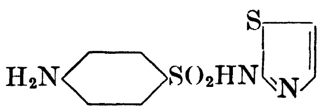
Like Dakin's solution it is a useful surgical germicide and has the added advantage of being more stable on storage as a dry powder.

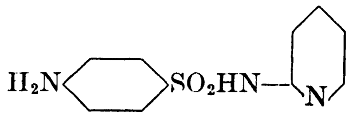
Hexylresorcinol is a powerful germicide with a high phenol coefficient (Table 2). It is made by the condensation of resorcinol and caproic acid and subsequent reduction.[2]



Sulfa Compounds.—The group of sulfur compounds familiarly known as *sulfa* drugs are recent arrivals in the germicidal field. They possess unique properties that make them especially valuable. Most germicides are applied externally, but the sulfa drugs and certain of the arsenicals may be administered internally. The more important members of this group are sulfonamide derivatives of aniline, pyridine, and thiazole and are prepared by a variety of methods.


Sulfanilamide


Sulfathiazole


Sulfapyridine

Metallic Compounds.—Only a few of the metals find use in germicidal compounds. Mercury, silver, and arsenic are the most widely employed.

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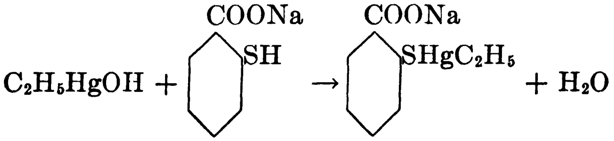
[1] "The Merck Index," 5th ed., Merck and Co., Rahway, N.J., 1940.

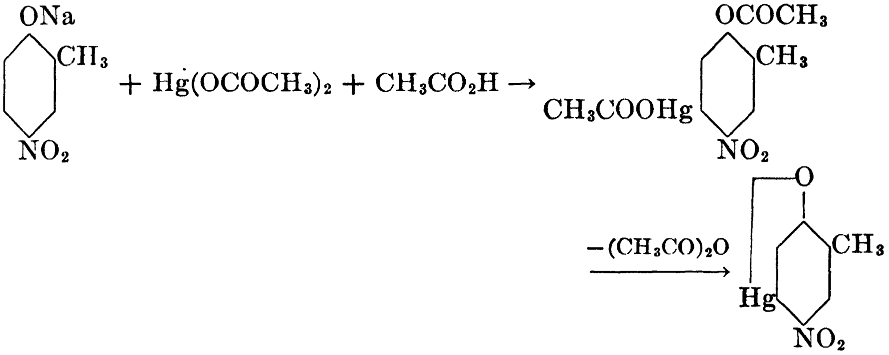
[2] GROGGINS, "Unit Processes in Organic Synthesis," 2d ed., p. 526, McGraw-Hill Book Company, Inc., New York, 1938.

Mercury Compounds.—Two of the more important mercurials are Merthiolate and Metaphen, both of which are excellent germicides. Merthiolate is sodium ethyl-mercurithiosalicylate and is made[1] as follows:

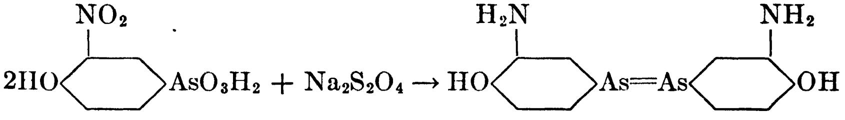
$$C_2H_5MgBr + HgCl_2 \rightarrow C_2H_5HgCl + MgBrCl$$
$$C_2H_5HgCl + NaOH \rightarrow C_2H_5HgOH + NaCl$$



Metaphen is the anhydride of 4-nitro-5-hydroxymercuri-2-methyl-phenol. It may be prepared by the following series of reactions:[2]



Arsenic Compounds.—The important arsenic compounds are arsphenamine (Salvarsan) and its many modifications (Neosalvarsan, etc.). They constitute the group of drugs used in the treatment of syphilis. Several preparations of Salvarsan are known, but one of the most common is to treat *m*-nitro-*p*-hydroxyphenyl arsonic acid with sodium hydrosulfite.



Salvarsan is sold as the dihydrochloride.

Silver Compounds.—Silver compounds are often employed as germicides. The application of a dilute solution of silver nitrate in the eyes of new-born babies is required by law in most states. Argyrol, a silver protein preparation, is used extensively for eye, ear, nose, and throat infections.

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[1] KHARASCH, U.S. Pats. 1589599 (1926); 1672615 (1928); for more details see Groggins, *op. cit.*, pp. 531–532.

[2] RAIZISS, U.S. Pat. reissue 17563; Can. Pat. 264444 (1926).

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CHAPTER XXVII

PERFUME AND FLAVORING INDUSTRIES

The particular cells that *perceive odors* are located near the top of the nasal cavity, quite close to the septum. As the ordinary process of breathing does not draw air over these regions, they soon would become dry and insensitive. By flaring the nostrils and sniffing, however, the inspired air is passed directly over the olfactory region where the conditions are optimum for discriminatory smelling. Since smell is a chemical sense, a contact is necessary for perception; and the substance, either gaseous or particulate, to be smelled must impinge on the moist surface of the region and dissolve. Since olfactory nerves are quickly fatigued, protracted smelling of any one substance will exhaust the power to recognize it, but the nerve endings may be easily rehabilitated by the breathing of fresh air again. Each odor has a *threshold value* depending on its intensity and volatility. Because of this, civet, when strong, has the disagreeable fecal odor of indole but, upon dilution, the indole passes below its threshold intensity and the warm flowery note of the civetone becomes apparent. Some odors that may appear intense are not so at all, as ammonia and formic acid; these compounds produce a sensation that may be likened to a mild pain and not to a true odor.

Historical.—The ancient and universal art of perfume compounding had its probable origin in the religious and ceremonial mysteries of the Egyptians. Aromatic incense and unguents were made by the priests for use in worship and regal funerals. The Jews carried the art with them out of Egypt, and specific directions for preparing a "holy unguent" may be found in the Bible.

After the conquest of Cleopatra and her people by the Romans, it was only natural that some of the customs and artifices of the Egyptians should follow the stream of grain that poured into needy Rome, and the sweet-smelling oils found high favor with the opulent portion of the populace. Soon both the Romans and the Greeks had gone to extremes in the application of this new-found divertissement. Every garment had a different odor. Horses and dogs were heavily perfumed. Doves treated with rare oils and costly fragrances were released at banquets and rained a gentle shower of scent upon the guests as they ate.

The returning Crusaders brought to Europe all the art and skill of the Orient in perfumery as well as information relating to the sources of gums, oils, and spices. René, perfumer to Catherine de' Medici, invented many new confections to delight the queenly nose and, in his spare time, was one of the cleverest and deadliest of the famous de' Medici poisoners. It may be said in defense of Catherine that she founded the flower perfume industry at Grasse. Paris was at this time and remained for some time the perfume capital of the world. For special occasions, 1,500 fountains in Paris flowed with exotically scented water. Madame de Pompadour used a different perfume every day and, out of her lavish budget, a paltry $100,000 a year was allotted to cosmetics and perfumery.

THE PERFUME INDUSTRY[1]

The two main changes that have taken place in the perfume industry since de' Medici's time are the introduction of synthetics and the improved methods of obtaining the true flower oils.

A perfume may be defined as any mixture of pleasantly odorous substances incorporated in a suitable vehicle. Formerly, practically all the products used in perfumery were of natural origin. Even when man first started imitating Nature and synthesizing materials for use in this field, he endeavored to duplicate the finest in Nature. There has been a marked tendency in recent years, however, to put on the market perfumes which have no exact counterpart in the floral kingdom but which are merely pleasing to the senses. These are the "fantasy" perfumes and have received wide acceptance. The finest modern perfumes are neither wholly synthetic nor yet completely natural. The best product of the art is a judicious blend of the two in order to enhance the natural perfume, to reduce the price, and to introduce new notes of fragrance into the enchanting gamut at present available. A product made solely of synthetics tends to be coarse and unnatural because of the absence of impurities in minute amounts which finish and round out the bouquet of the natural odors. The chemist has also succeeded in creating floral essences of flowers which yielded no natural essence or whose essence was too expensive or too fugitive to make its extraction profitable. Lily of the valley, lilac, and violet are examples.

Perfume gains its name from the fact that in its original form it was incense in the Egyptian temples (*perfumare*—to fill with smoke). The early incenses were merely mixtures of finely ground spices held together by myrrh or storax. The next advance was the discovery that, if certain spices and flowers were steeped in fat or oil, the fat or oil would retain a portion of the odoriferous principle. Thus were manufactured the ointments and fragrant unguents of Biblical fame. To Avicenna, the Arabian physician, must go the honor of discovering steam distillation of volatile oils. During his search for medical potions, he found that flowers boiled in an alembic with water gave up some of their essence to the distillate.

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[1] REDGROVE, Some Fundamentals of Perfumery, *Pharm. J.* **131**, 395, 452 (1933).

The constituents of perfumes are threefold: the vehicle or solvent, the fixative, and the odoriferous elements.

VEHICLE

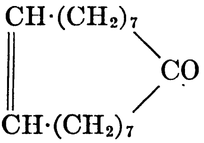
The modern solvent for blending and holding perfume materials is a special highly refined ethyl alcohol mixed with more or less water according to the solubilities of the oils employed. This solvent, with its volatile nature, helps to project the scent it carries, is fairly inert to the solutes, and is not too irritating to the human skin. The slight natural odor of the alcohol is removed by deodorizing or "prefixation" of the alcohol. This is accomplished by adding a small amount of gum benzoin or other resinous fixatives to the alcohol and allowing it to mature for a week or two. The result is an almost odorless alcohol, the natural rawness having been neutralized by the resins.

FIXATIVE

In an ordinary solution of perfume substances in alcohol, the more volatile materials will evaporate first, and the odor of the perfume will consist of a series of impressions rather than the desired ensemble. To obviate this difficulty, a fixative is added. Fixatives may be defined as substances which are of lower volatility than the perfume oils and which retard and even up the rate of evaporation of the various odorous constituents. The types of fixative to be considered are animal secretions, resinous products, essential oils, and synthetic chemicals. Any of these fixatives may or may not contribute to the odor of the finished product but, if they do, they must blend with and complement the main fragrance.

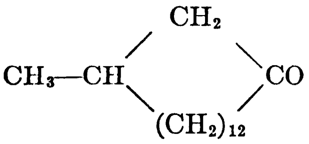
Animal Fixatives.—*Ambergris* is a pathological secretion or calculus found in the intestine of the male sperm whale. It is obtained by cutting open the captured whale, or it is found floating in the ocean or stranded on a beach. It supposedly originates from an irritation upon the intestinal mucosa, caused by cuttlefish beaks in the whale's diet. It is waxy in consistency, softening at about 60°C. Its color may be white, yellow, brown, black, or variegated like marble. It is composed of 80 to 85 per cent ambrain, resembling cholesterol and acting merely as a binder, and 13 to 15 per cent of ambergris oil, which is the active ingredient. It is employed as an alcoholic tincture which must be matured before it is used. The odor of the tincture is decidely musty, and it has great fixative powers.

Civet is the soft fatty secretion of the perineal glands of the civet cats which are mainly indigenous to Abyssinia and India. The cats are 2 or 3 ft. long and are spotted brown and black. They are kept in captivity in pens in which the temperature is higher than normal because of covering and exposure to the hot sun. The heat and also the teasing of the cat are said to increase the yield of the civet. The secretions are collected about every 4 days by spooning and are packed for export in hollowed horns. The crude civet is disagreeable in odor because of the indole present. On dilution and aging, however, the indole odor disappears, and the sweet and somewhat floral odor appears. This is due to civetone, a cyclic ketone of this composition:



The civet is employed as a fixative either in a tincture or as an absolute. Its use along with musk is quite common. *Castor* is a brownish orange exudate of the perineal glands of the beaver. It is obtained chiefly from Siberia and Canada. It is employed as a tincture, but its use is not so common as that of the other animal fixatives.

Musk is the dried secretion of the preputial glands of the male musk deer, found in the Himalayas. The deer are killed and the musk is excised in pods the size of a crab apple and dried. The product in the natural cover is called *pod musk,* while that which has been removed and dried is known as *grain musk.* The odor is due to a cyclic ketone of the following composition:



This compound, called *muskone,* is present to the extent of from ½ to 2 per cent. Musk, the most useful of the animal fixatives, will impart body and smoothness to a perfume composition even when diluted so far that its own odor is completely effaced. Musk is used for its own sake in heavy Oriental perfumes. Around the Gulf of Adalia in Asia Minor are large tracts of *Liquidambar orientalis,* a tall tree from which *storax* is obtained. The trees are bruised, and the inner bark is removed and boiled with water to free the balsam. It is a solid brown substance and is usually purified by solution in alcohol, filtering, and concentrating. The active ingredients are esters of cinnamic acid, chiefly cinnamyl cinnamate.

Resinous Fixatives.—The resinous fixatives are normal or pathological exudates from certain plants. Nonvolatile resinous exudates are called *resins.* Those containing gum are known as *gum resins,* while those containing a volatile essential oil are *oleoresins.* The solid products obtained by solvent extraction of the resins and subsequent concentration of the resulting solutions are sold as *resinoids.* These are stronger and more uniform in composition and easier to employ than the corresponding resins from which they are made. They are normally designated by a capitol R, *i.e.*, the resinoid of benzoin would be benzoin R. The following are among the commercially important resinous fixatives:

Peru balsam is an oleoresin obtained as a thick brown liquid from *Myroxylon pereirae,* a tree growing in San Salvador. The bark of the tree is alternately wounded and burned, thus producing several flows of the balsam of different and diminishing qualities. The effluent liquid is collected on rags, which are then boiled in water to remove the balsam. The principal constituents are the benzoic and cinnamic acid esters of benzyl alcohol and peruviol, cinnamic acid, coumarin, and vanillin.

Tolu balsam is a reddish-brown, soft, tacky substance becoming hard and brittle on aging. It is gathered from *Myroxylon toluiferum,* a tree growing mainly in Colombia, by incision of the bark and collection of the exudate in gourd cups much after the manner of getting latex from rubber trees. It contains benzoic and cinnamic acids and their benzyl esters along with vanillin and considerable amounts of resins.

The gum resin, *olibanum,* takes its name from Lebonah, the classical Lebanon, land of milk and honey, and is identical with the Biblical frankincense. Repeated gashes are made in the bark of *Boswellia carteri,* a tree indigenous to Somaliland and Arabia, and the gum is collected in hard, yellow, transparent tears. They have a slight odor and are used widely in incense as well as for their fixative properties. The chief constituents are pinene, phellandrene, and dipentene.

Benzoin is a reddish-brown, translucent resin produced from incisions in the tree, *Styrax benzoin.* Although it is found in Java, Sumatra, Penang, and Siam, only the last variety is fine enough for high-class perfume use. Gum benzoin from Siam contains almost half its weight of free and combined benzoic acid, which was first prepared by sublimation of the gum to give "flowers of benzoin." The benzoin also may contain styrol and vanillin. An old synonym occasionally met with is *gum benjamin.*

Essential Oil Fixatives.—A few essential oils are used for their fixative properties as well as their odor. The more important of these are clary sage, vetiver, patchouli, orris, and sandalwood. These oils have boiling points higher than normal (285 to 290°C.).

Synthetic Fixatives.—Certain high-boiling comparatively odorless esters are used as fixatives, to replace some of the imported animal fixatives. Among them may be mentioned glyceryl diacetate (259°C.), ethyl phthalate (295°C.), and benzyl benzoate (323°C.). Other synthetics are used as fixatives although they have a definite odor of their own that contributes to the ensemble in which they are used. A few of these are listed:

Amyl benzoate
Phenylethyl phenylacetate
Cinnamic alcohol esters
Cinnamic acid esters
Acetophenone[1]
Musk ketone
Musk ambrette
Benzophenone
Vanillin
Coumarin
Heliotropin
Hydroxycitronellal
Indole
Skatole

ODOROUS SUBSTANCES

Most odorous substances used in perfumery come under three headings: (1) essential oils, (2) isolates, and (3) synthetic or semisynthetic chemicals.

1. Essential Oils.—An essential oil may be defined as a volatile, odoriferous oil of vegetable origin. The distinction should be made, however, between the natural flower oils which are obtained by enfleurage or solvent extraction and the essential oil recovered by distillation. The distilled oils may lack some component which is not volatile enough or which is lost during the distillation. Two notable examples of this are rose oil in which the phenylethyl alcohol is lost to the watery portion of the distillate, and orange-flower oil in which the distilled oil contains but a very small proportion of methyl anthranilate while the extracted flower oil may contain as much as one sixth of this constituent.

The essential oils are in the main insoluble in water and soluble in organic solvents, although enough of the oil may dissolve in water to give an intense odor to the solution as in rose water and orange-flower water. The oils are flammable liquids which are volatile enough to distill unchanged in most instances. They are also volatile with steam. They vary from colorless to yellow or brown in color. An essential oil is usually a mixture of compounds, although oil of wintergreen is almost pure methyl salicylate. The refractive indexes of the oils are high, averaging around 1.5. The oils show a wide range of optical activity, rotating in both directions.

The compounds occurring in essential oils may be classified as follows:

1. Esters: Mainly of benzoic, acetic, salicylic, and cinnamic acids.
2. Alcohols: Linaloöl, geraniol, citronellol, terpinol, menthol, borneol.
3. Aldehydes: Citral, citronellal, benzaldehyde, cinnamaldehydes, cuminic aldehyde, vanillin.

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[1] Acetophenone should be used with great caution because of its powerful odor which tends to protrude above all others.

TABLE 1.—IMPORTANT ESSENTIAL OILS

Name of oil	Botanical source	Geographical source	Method of production	Part of plant used	Chief constituents
Allspice (pimento)	*Pimenta officinalis, L.*	Jamaica	Steam	Berries	Eugenol 70 %
Anise	*Pimpinella anisum, L.*	Spain, Russia, Germany	Steam	Seed	Anethole 90 %
Bay	*Laurus nobilis, L.*	West Indies	Steam	Leaves	Eugenol 50 %
Bergamot	*Citrus bergamia*	Southern Italy	Expression	Peel	Linalyl acetate 40 %, linaloöl 6 %
Bitter almond	*Prunus amygdalus*	California, Mexico	Steam	Seeds	Benzaldehyde 96–98 %, HCN 2–4 %
Cajuput	*Melaleuca minor*	Moluccas, Malay, Persia	Steam	Leaves and twigs	Cineole (eucalyptole) 50–60 %
Calamus (sweet flag)	*Acorus calamus, L.*	India, Java	Steam	Rhizome	Asaron, acetic and heptylic esters
Cananga	Second grade of ylang-ylang *q.v.*				
Caraway	*Carum carvi, L.*	Northern Europe, Holland	Steam	Seed	Carvone 55 %, *d*-limonene
Cardamon	*Elettaria cardamomum*	India, Ceylon	Steam	Seed	Cineole, terpinyl acetate, limonene
Cassis (Chinese cinnamon)	*Cinnamomum cassia*	China	Steam	Leaves and twigs	Cinnamic aldehyde 80–90 %, cinnamyl acetate
Cedarwood	*Juniperus virginiana, L.*	North America	Steam	Shavings	Cedrene, cedral
Cinnamon	*Cinnamomum zeylanicum, Nees*	Ceylon	Steam	Bark	Cinnamic aldehyde 60 %, eugenol 8 %, phellandrene
Citronella	*Andropogon*	Java, Ceylon	Steam	Grass	Geraniol 60–90 %, citronellal
Clove	*Eugenia aromatica*	Zanzibar, Moluccas	Steam	Buds (cloves)	Eugenol, 85–95 %
Coriander	*Coriandrum sativum, L.*	India, Central Europe, Levant	Steam	Seeds	Linaloöl, pinene
Eucalyptus	*Eucalyptus globulus*	California, Australia	Steam	Leaves	Cineole (eucalyptole) 70–80 %
Fennel	*Foeniculum capillaceum*	Central Europe, Egypt, Asia Minor, Persia, India, Japan	Steam	Fruit	Anethole 50–60 %, fenchone 20 %
Geranium	*Pelargonium graveolus*	Mediterranean countries	Steam	Leaves	Geraniol esters 30 %, citronellol
Grapefruit (shaddock)	*Citrus paradisi*	Florida, Texas	Expression	Peel	Limonene 90 %
Jasmine	*Jasminum grandiflorum, L.*	Grasse	Cold pomade or solvent extraction	Flowers	Benzyl acetate, linaloöl, and esters
Juniper	*Juniperus communis, L.*	Hungary, Italy	Steam	Berries	Pinene, cadinene
Lavender	*Lavandula spica, L.*	France, England	Steam	Flowers	Linalyl acetate 30–40 %
Lemon	*Citrus limonum*	Sicily, California	Expression	Peel	*d*-Limonene 90 %, citral (3.5–5 %)
Lemon grass (verbena)	*Andropogon citratus*	Ceylon, Java, West Indies	Steam	Grass	Citral 80 %

TABLE 1.—IMPORTANT ESSENTIAL OILS.—(*Continued*)

Name of oil	Botanical source	Geographical source	Method of production	Part of plant used	Chief constituents
Lime	***Citrus medica, L.***	Italy, Mexico, West Indies, Florida	Expression	Peel	Linalyl acetate, citral
Linaloa (bois de rose)	....	French Guiana	Distillation	Wood	Linaloöl (high), geraniol, terpineol
Narcissus	***Narcissus tazetta***	Holland, Grasse	Pomade, solvent extraction	Flowers	
Neroli (sweet orange flower)	***Citrus aurantium, L.***	France, Portugal	Steam, solvent extraction	Flowers	Linaloöl and esters 20 %, methyl anthranilate
Nutmeg (nutmeg butter)	***Myristica fragrans***	Moluccas	Distillation	Seed (nutmegs)	Myristicin, pinene
Orange peel, bitter	***Citrus aurantium, L.***	California, Florida, Mediterranean countries	Expression	Peel	*d*-Limonene 90 %
Patchouli	***Pogostemon patchouly***	Malay	Steam	Leaves	Patchouli alcohol, cadinene
Peppermint	***Mentha piperita, L.***	Japan, England, Michigan, Oregon, New York, Indiana	Steam	Leaves and tops	Menthol 45–90 % and esters, menthone
Pine needle	***Abies sibirica***	Siberia	Steam	Needles	Bornyl acetate 40 %
Rose	***Rosa damascena, Rosa gallica***	Bulgaria	Steam, solvent extraction, enfleurage	Flowers	Geraniol and citronellol 75 %
Rosemary	***Rosmarinus officinalis, L.***	France, Spain	Steam	Flower or leaves	Borneol 10 %, cineole, pinene
Sage	***Salvia officinalis, L.***	Dalmatia	Steam	Leaves	Thujone, cineole
Sandalwood	***Santalum album, L.***	Mysore	Steam	Wood	Santalol 90 %, santalol esters 3 %
Sassafras	***Sassafras officinalis***	Atlantic seaboard	Steam	Root, wood, bark	Safrole 80 %, eugenol
Spearmint	***Mentha viridis, L.***	Michigan, Indiana	Steam	Leaves	Carvone 40–60 %
Star anise (badian)	***Illicium verum***	French Indo-China, Tonquin district	Steam	Fruit	Anethole 90 %
Thyme	***Thymus vulgaris, T. algeriensis***	France, Algiers, Spain	Steam	Plant	Thymol and carvacrol 20–40 %
Tuberose	***Polianthes tuberosa, L.***	France	Enfleurage, solvent extraction	Flowers	
Vetiver (cuscus)	***Andropogon muricatus***	India, Ceylon, Réunion	Steam	Roots	Vetivene, vetivenol
Violet	***Viola odorata, L.***	France	Cold solvent extraction	Flowers, leaves	
Wintergreen (gaultheria)	***Gaultheria procumbens, L.***	Pennsylvania, Kentucky, Tennessee	Steam	Leaves	Methyl salicylate 99 %

4. Acids: Benzoic, cinnamic, myristic, isovaleric acids in the free state.
5. Phenols: Eugenol, thymol, carvacrol.
6. Ketones: Carvone, menthone, pulegone, irone, fenchone, thujone, camphor, methyl nonyl ketone, methyl heptenone.
7. Ethers: Cineole[1] (eucalyptole), anethole, safrole.
8. Lactones: Coumarin.
9. Terpenes: Camphene, pinene, limonene, phellandrene, cedrene.
10. Hydrocarbons: Cymene, styrene (phenylethylene).

Although the part played by essential oils in the life of plants is somewhat obscure, they are probably connected with metabolism, fertilization, or protection from enemies. The oils may occur in intercellular spaces or in oil sacs. Any or all parts of the plant may contain an oil. Essential oils are found in the buds, flowers, leaves, bark, stems, fruits, seeds, wood, roots, and rhizomes, and in some trees in the oleoresinous exudates.

The volatile oils may be recovered from the plants by a variety of methods:[2] distillation, expression, maceration, enfleurage, and extraction by volatile solvents. The yield based on 5 tons of crude material will vary from 5 oz. of violet oil to 1,800 lb. of clove oil.

Distillation, Usually with Steam.—In order that the steam may more easily remove the oil, some treatment of the material may be required. Flowers and grasses are normally charged into the still without preparation. Leaves and succulent roots and twigs are cut up into small pieces. Dried materials are powdered. Woods and tough roots are chipped in a revolving hogger. Seeds and nuts are fed through crushing rolls which are spaced so as to crack them. Berries are charged in the natural state, as the heat of distillation soon develops enough pressure to burst their integument. The charge should not be too finely comminuted, or it will pack down solidly in the still and the steam applied will channel rather than reach the whole mass evenly.

The stills employed in factories are of copper, tin-lined copper, or stainless steel and of about 600 gal. capacity. They are provided with condensers of various sorts, the tubular ones being the more efficient and with a separator for dividing the oily layer from the aqueous one. Although removable baskets for holding the material to be distilled are used, the better procedure seems to be to construct the still with a perforated false plate, lying just above the bottom. Underneath this false bottom are the steam coils, both closed and perforated. Manholes should be provided at the top and just above the false bottom for an inlet and outlet of the material to be distilled. Such a still will handle from 250 to 800 lb. of material. If the charge is finely ground or easily packed material, the still should be provided with a powerful stirrer, in which case the lower manhole may be omitted and the spent material blown out through a bottom valve. In operating these stills, the charge is heated by steam in both the closed and the open pipes, this effecting an economical steam distillation. The aqueous layer in the condensate frequently carries, in solution, valuable constituents as from rose and orange-flower oil and is consequently pumped back into the still to supply some of the necessary water. Steam distillation is carried out for the most part at atmospheric pressure. If the constituents of the oil are easily subject to hydrolysis, however, the process may be run in a vacuum.

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[1] This is an *internal* ether.

[2] SIEVERS, Extracting Volatile Oils from Plants, *U.S. Dept. Agr. Tech. Bull*, **16** (1928); RHODES, Perfume, *Mfg. Perfumer*, **3**, 6–9 (1938).

Much distillation for essential oils is done at the harvest site in extremely crude stills. These are converted oil drums or copper pots equipped with pipe condensers running through tubs of water. The material and water are charged into the still and a direct fire is built underneath of dried material exhausted in previous distillations. The efficiency is low and the oil is contaminated with pyrolysis products such as acrolein, trimethylamine, and creosotelike substances.

The crude oils obtained from the stills are sometimes further treated before use by rectification under vacuum, fractional freezing (menthol from Japanese peppermint oil), by washing with potassium hydroxide to remove free acids and phenolic compounds, by removal of wanted or unwanted aldehydes and ketones through formation of the bisulfite addition compounds, or by formation of specific insoluble products as in the reaction of calcium chloride with geraniol.[1]

Expression.—Expression[2] is used to free the oil from the peels of the lemon, lime, orange, grapefruit, and bergamot, either by hand or machine pressing.

In the former procedure the peel is trimmed from the fruit in three sections. Each of these is turned inside out against an ordinary sponge, ejecting the oil into the sponge which is periodically squeezed dry. One man can prepare only 24 oz. of lemon oil a day by this method, but the oil is of the highest quality. An alternate hand method occasionally encountered is the use of a hemispherical bowl lined with short spikes and equipped with a hollow handle. The whole fruit is rolled around against the spikes, puncturing the oil cells and allowing the oil to collect in the handle.

Many machines have been invented to take the place of the hand labor in pressing out the citrus oils. They are all about the same in principle. The fruit is tumbled or forced against a grating surface of metal or glass either under water or in a spray of water. The debris abraded from the surface is filtered or centrifuged out and the oil separated from the water by decantation or with a separator such as made by De Laval or Sharples. The oil-saturated rinse water is reused. Oxidation of the oil, difficulty in handling odd sizes of fruit, and the fact that the hand-pressed is decidely superior in quality have all militated against widespread introduction of these machines.

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[1] JONES and WOOD, Preparation of Pure Geraniol, *Ind. Eng. Chem.*, **34**, 488 (1942).

[2] GUENTHER, Italian Oil of Lemon, *Am. Perfumer*, **25**, 9–13 (1930).

The albedo, or white portion of the rind in citrus fruits, when dried may be made to yield about 35 per cent of its weight of commercial pectin, much of which enters the jelly industry. The exhausted rinds are dried and sold as a feed, and the fruit itself goes into natural citric acid. As a rule the better appearing fruits are sold as food, so that the culls go into oil or juice.

Maceration.—The flowers are sometimes ground and placed in linen bags which are steeped in molten fat or bland oil at about 70°C. until the fat is saturated with the flower perfume. The bags and flowers are freed from excess fat clinging to them by pressing in a hydraulic press. The fat is allowed tó cool and is then extracted with alcohol which dissolves all of the perfume material and a little of the fat. The fat is removed by chilling and filtering the alcoholic solution. This solution is known as an *extract.* If the alcohol is removed under vacuum, the residue is an *absolute.* The used fat is sold to soapmakers.

Enfleurage.—The enfleurage process is a cold-fat extraction method. The enfleurage fat is composed of 40 parts of beef tallow and 60 parts of lard. These are melted together and repeatedly beaten under cold water and alum solutions to purify them. Benzoin is added to the fat mixture to preserve it.

The process is carried out by loading the "chassis" or frames. Each chassis is a plate of glass about 2 ft. square encased in a wooden frame. The previously prepared fat is spread in a ⅛-in. layer on each side of the glass. Flowers are pressed into the surface of the fat on one side of the frame only and the frames are stacked vertically so that each layer of flowers almost touches the layer of fat on the underside of the frame above it. The frames are left in this position from 1 to 3 days, when the exhausted flowers are stripped from the fat either by hand or by revolving brushes. Fresh flowers or petals are placed on the other side of the frame, and the frames are again stacked. This is repeated from thirty to thirty-five times, or until the fat is saturated, a point that is known from long experience. The saturated fat is called a *pomade.*

The fat is removed from the frames and extracted with alcohol to recover the perfume. This alcoholic solution is cooled and filtered to remove the slight amount of fat that has dissolved. The alcohol solution is the *extract* and the residue after evaporation of the solvent is the *enfleurage absolute* similar to the products in the maceration process.

The lower temperatures in the enfleurage process are better suited to the production of delicate oils than the maceration method. Also, especially in the case of tuberose and jasmine flowers, the picked flowers continue to produce perfume as long as they are alive. The enfleurage permits this production to go to completion, whereas the maceration merely extracts the odor principle present in the blossom at the time of harvest.

Extraction with Volatile Solvents.—The solvent desirable for essential oil extraction should take up the oil selectively and dissolve a minimum quantity of wax, resin, and color. The solvent should be low-boiling, chemically inert to the constituents of the oil and should evaporate completely without leaving any odorous residue. The following liquids have been recommended: methanol, ethyl alcohol, carbon bisulfide, chloroform, ethyl ether, methyl chloride, acetone, benzene, and petroleum ether. The most widely used of these is petroleum ether or low-boiling gasoline which consists of a mixture of pentane, hexane, and heptane in varying proportions.

The flowers are placed in a removable basket in the extraction chamber of a commercial Soxhlet extractor. The petroleum ether is boiled in a still underneath, and the vapors arise, are condensed, and allowed to flow through the charge, picking up some of the soluble portions and dropping back into the ether still. In this way the flowers are treated with fresh cool solvent until they are exhausted. Then the condenser connection is changed and the solvent boiled off of the soluble material that has gathered in the still pot.

In a more widely used process the oil is extracted by a battery of extractors working on the *countercurrent principle.* There are three drums to a battery, each holding about 350 gal. The drums revolve around a horizontal axis and are divided into segments by perforated plates at right angles to the axis. Each drum is steam-jacketed. About 300 lb. of flowers are charged into the first drum along with 150 gal. of petroleum ether which has already come through the other two drums The drum and its contents are rotated for an hour cold and for an additional half hour with steam in the jacket. The saturated solvent is pumped to the recovery still, the flowers in the drum are treated twice more, the second time with once-used solvent and the last time with fresh solvent from the recovery still. The exhausted flowers are blown with steam to recover the adhering solvent. About 90 per cent of the solvent is boiled off at atmospheric pressure and the rest is removed under vacuum.

After the solvent is removed in either process, the semisolid residue contains the essential oil along with a quantity of waxes, resins, and coloring material from the blossoms. This pasty mass is known as the *concrete.* It, in turn, is treated with cold alcohol in which most of the wax and resin is insoluble. The small amount of unwanted material that does dissolve is removed by cooling the solution to −20°C. and filtering it. The resulting liquid contains the essential oil and some of the ether-soluble color of the flower and is known as an *extract.* When the alcohol has been removed, an *absolute* remains. As might be expected, there is considerable difference among the absolutes prepared from the same flower by the three methods enumerated: maceration, enfleurage, and extraction with a volatile solvent. For each flower, there is an optimum method that produces the best absolute for any given purpose.

In some oils there is a large quantity of terpenes. This is especially true in the case of lemon and orange oils with as much as 90 per cent *d*-limonene in their normal composition. Not only are terpenes and sesquiterpenes of *exceedingly* little value to the strength and character of the oils, but they oxidize and polymerize rapidly on standing to form compounds of a strong turpentinelike flavor. Furthermore the terpenes are insoluble in the lower strengths of alcohol used as a solvent and make cloudy solutions which are cleared up only with difficulty. For these reasons it is desirable to remove terpenes and sesquiterpenes from many oils. Such an oil, in the case of orange for example, is forty times as strong as the original and makes a clear solution in dilute alcohol. The oil has now very little tendency to rancidify, although it has not quite the freshness of the original. These treated oils are labeled "t.s.f." (terpene and sesquiterpene free).

An essential oil may be made *terpeneless* or at least have its terpenes reduced by a number of methods. The oil, such as that from limes, may be redistilled under a high vacuum through a good rectifying column. The terpenes come over first, then the odoriferous constituents, and finally the sesquiterpenes.

The oil may be charged into a still with 35 to 40 per cent *alcohol.* Upon distillation the condensate separates into two layers with the insoluble terpenes on top and the mixture of alcohol and the more volatile of the oil constituents in the bottom layer. When the terpenes have all come over, the top layer is decanted and the distillation continued until the odorous material is all distilled. The still residue will contain most of the sesquiterpenes. The terpenes can also be greatly reduced by selective washing methods as are satisfactory for oils of orange and lemon.

Because of the complex nature and the high price commanded by so many of the essential oils, there is a great deal of *adulteration* or sophistication practiced. These additions are extremely hard to detect in most cases as, whenever possible, a mixture of adulterants is used that does not change the physical constants of the oil. Common agents used are alcohol, cedar oil, turpentine, terpenes, sesquiterpenes, and the low-specific-gravity liquid petroleums. The advent of so many esters of glycol and glycerol on the market has increased the difficulty of detection as these are colorless, practically odorless, and in the right combination can be made to simulate almost any specific gravity and refractive index specifications set up for the oil they are intended to adulterate. Rose oil is sophisticated with geraniol or a mixture of geraniol and citronellol; wintergreen and sweet birch oil are mixed with large amounts of synthetic methyl salicylate; and lemon oil is often "stretched" considerably with citral from lemon-grass oil.

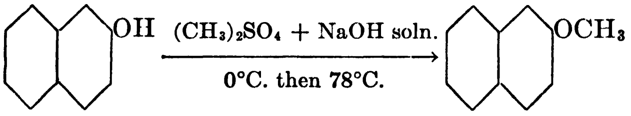
2. Isolates.—An isolate is a pure chemical compound whose source is an essential oil or other natural perfume material. Notable examples are eugenol from clove oil, pinene from turpentine, anethole from anise oil, and linaloöl from linaloa oil (bois de rose).

3. Synthetics and Semisynthetics Used in Perfumes and Flavors.—More and more important constituents of perfumes and flavors are being made by the usual chemical synthetic procedures. Some constituents are being chemically synthesized from an isolate or other natural starting materials and are classed as semisynthetics. Examples are vanillin prepared from eugenol from clove oil, ionone prepared from citral from lemon-grass oil, and camphor from turpentine. The following embrace some of the significant synthetics of this field. The better to correlate the manufacturing methods and apparatus with other like processes, the examples here presented are grouped under the most important unit process.

ALKYLATION PROCESSES

Ethyl vanillin or *bourbonal* possesses a finer and more intense vanilla odor than vanillin itself. It is manufactured by ethylating with diethyl sulfate in the last step in the making of vanillin from safrole.

Nerolin or *β-naphthyl methyl ether* is used in perfumes, imparting an odor resembling orange blossoms. It is made by the alkylation of β-naphthol.[1]



Yield 65 to 73 per cent

CONDENSATION PROCESSES

Salicylaldehyde is used in perfumery for its bitter almond odor, and for synthesis into coumarin. It also has antiseptic properties. It is manufactured from sodium phenate by heating with chloroform and caustic soda according to the Reimer-Tiemann reaction as outlined in the flow sheet of Fig. 1 and in the following formulations:

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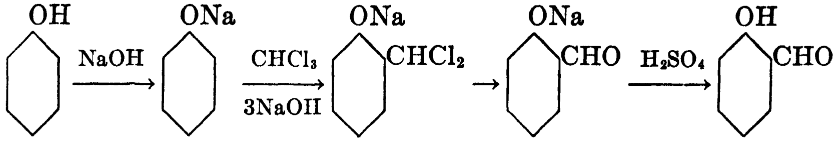
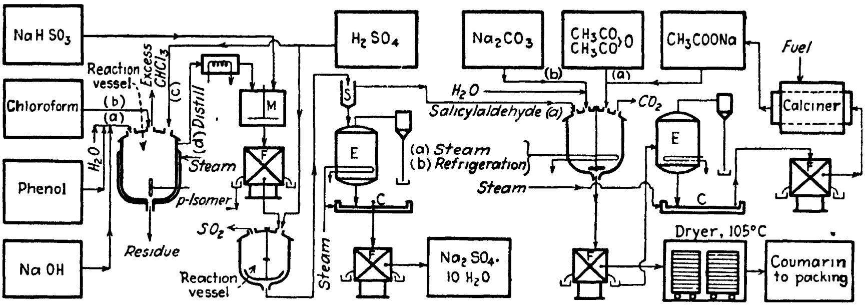
[1] CONANT, "Organic Syntheses," Vol. 9, p. 12, John Wiley & Sons, Inc., New York, 1929.



The crude salicylaldehyde contains some para isomer and other impurities. After acidification it is distilled from the reactor and purified through the solid sodium bisulfite compound. This is filtered off, decomposed with sulfuric acid, and the aldehyde (an oil) separated from the sodium sulfate.

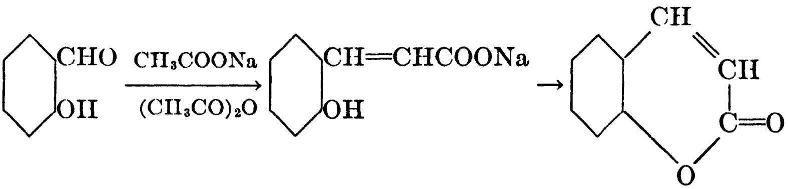


Key -- C, *crystallizer*; E, *evaporator*; F, *filter*; M, *mixer*, S, *separator*

Phenol	150 lb	Sodium acetate	25 lb	To produce coumarin, 100 lb or salicylaldehyde, 75 lb
Chloroform	25 lb	Sodium carbonate	40 lb	
Caustic soda	75 lb.	Steam	150 lb	
Sulfuric acid	95 lb	Refrigeration (ice equiv)	200 lb	
Sodium bisulfite	50 lb	Electricity	45 kw-hr	
Acetic anhydride	75 lb	Direct labor	4 man-hr	

FIG. 1.—Flow sheet for salicylaldehyde and coumarin.

Coumarin occurs in tonka beans and other plants, but it is made synthetically. It is employed as a flavor for tobacco, butter, medicines, and lemonade; it is also of importance in perfumes, having the odor of new-mown hay. It is manufactured from salicylaldehyde and sodium acetate according to the Perkin reaction as shown in Fig. 1 and the following equations wherein the Perkin reaction takes place at the boil, followed by neutralization with soda-ash solution and cooling to separate and crystallize the coumarin. This latter is filtered off, purified if necessary, and dried.[1]



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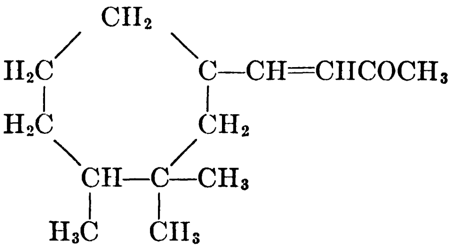
[1] ULLMANN, Enzyklopaedie der technischen Chemie, 2d ed., vol. 8, p. 843, Urban & Schwarzenberg, Berlin and Vienna, 1928–1932.

Diphenyl oxide has long been used in soaps because of its agreeable geranium odor and its stability against alkali. It is obtained as a by-product in the manufacture of phenol from chloro-benzene and caustic soda.

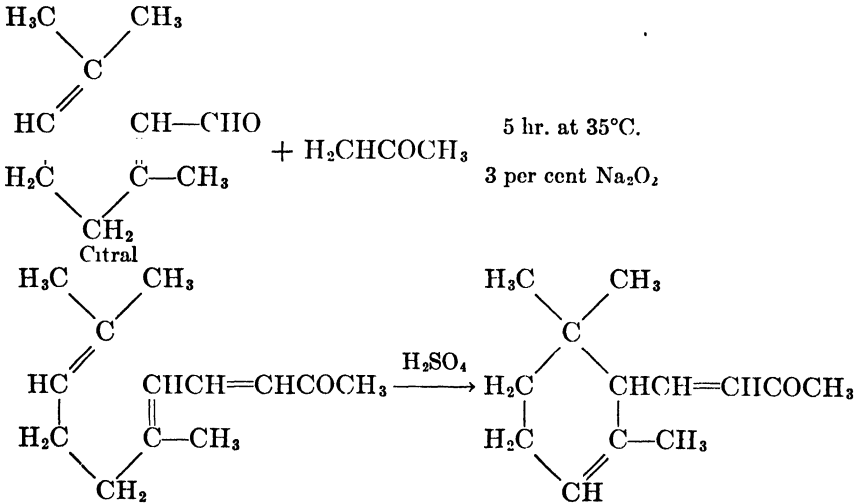
$$C_6H_5ONa + ClC_6H_5 \xrightarrow[300^\circ\text{C.}]{4{,}000\text{ lb.}} C_6H_5OC_6H_5 + NaCl$$

Ionone in its commercial form contains variable proportions of α-ionone and β-ionone, and comprises the odorous principle of artificial violet perfumes and orris root. The true violet odor is due to β-irone, a similar but seven-membered ring compound.



β-Irone

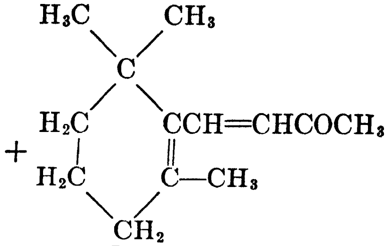
The mixed isomers of α- and β-ionone are made by an ordinary aldol condensation of citral with acetone yielding pseudo-ionone. This is followed by an acid ring closure and separation of the isomers, if desired, by means of sodium bisulfite compounds of which the α- is less soluble in sodium chloride solution.



Citral

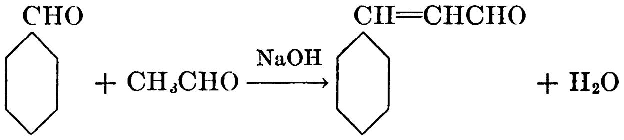
Pseudo-ionone

α-Ionone



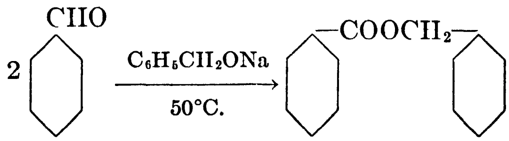
β-Ionone

Cinnamic aldehyde has a cinnamon odor. As it oxidizes in air to cinnamic acid, it should be protected from oxidation. Although this aldehyde is obtained from Ceylon and Chinese cinnamon oils, it is synthesized by action of alkali upon a mixture of benzaldehyde and acetaldehyde.



ESTERIFICATION PROCESSES

Benzyl benzoate has a faint aromatic odor, boils at 323 to 324°C., and is a fixative. It is also used in chewing-gum flavors. It occurs in Peru and tolu balsams but it prepared synthetically from benzaldehyde by the catalytic action of sodium benzylate, or $Al(OC_2H_5)_3$.



GRIGNARD PROCESSES

Phenylethyl alcohol has a roselike odor and occurs in the volatile oils of rose, orange flowers, and others. It is an oily liquid and is much used in perfume formulation, over 150,000 lb. being sold annually. Phenylethyl alcohol can be made by a number of procedures; that employing the Grignard[1] reaction is probably a rare industrial application of this reaction.

One hundred fifty parts of magnesium turnings are refluxed with 3,500 parts of chloro-benzene and reacted with 200 parts of ethylene oxide in 300 parts of benzene. Acidulation breaks the addition product into β-phenylethyl alcohol and a magnesium salt.

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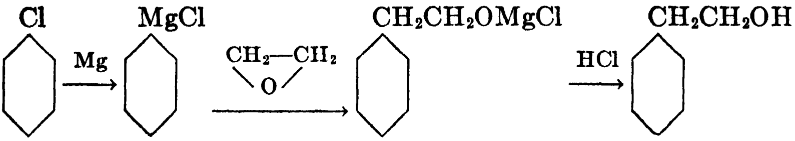
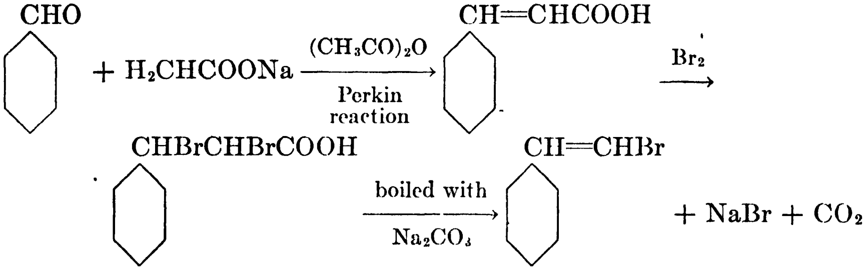
[1] BRITTON, How Dow Synthesizes Phenylethyl Alcohol, *Manuf. News*, **16**, No. 2, 23 (1941).



HALOGENATION PROCESSES

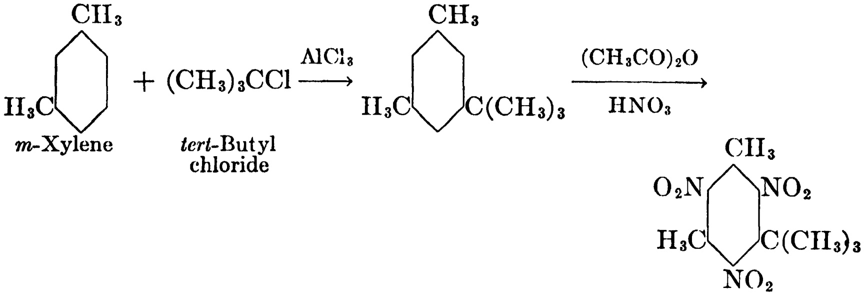
β-Bromostyrene has a harsh, powerful hyacinth odor. (The α-bromostyrene is a lachrymator.) This compound is made by the following sequences from benzaldehyde through cinnamic acid:



NITRATION PROCESSES

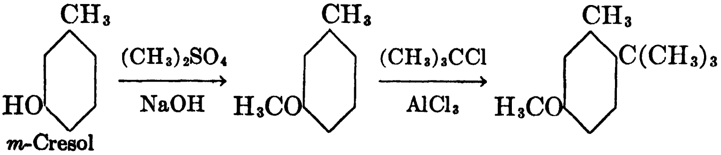
Artificial musks comprise a number of products that are not identical with the natural musk. These are acceptable substitutes for this fixative and over 90,000 lb. are manufactured annually. While a musk fixative is synthesized from toluene, the reaction from xylene and *m*-cresol are here given for two of the commercial products.

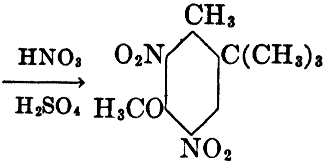
Xylene Musk:



Xylene musk

Musk Ambrette:





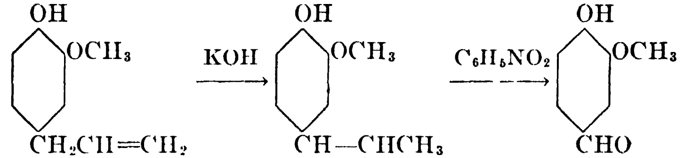
Musk ambrette

OXIDATION PROCESSES

Phenyl-acetaldehyde is used in producing lilac and hyacinth perfumes. This product, $C_6H_5CH_2CHO$, is made by oxidizing phenylethyl alcohol with chromic acid.

Vanillin is one of the most widely used flavors, being manufactured to the extent of more than 600,000 lb. per year. Its characteristic flavor is known to all. It is also used as a fixative in perfumery. For its manufacture many processes have been employed of which the following are important:

1. From eugenol from oil of cloves, through isoeugenol followed by oxidation to vanillin using nitro-benzene as the oxidizing agent.



Eugenol Isoeugenol Vanillin

2. From safrole from camphor oil through isosafrole to protocatechuic aldehyde followed by methylation (ethylation gives the homolog, ethyl vanillin).
3. From lignin[1] through an alkaline pressure cook at 150 lb. for several hours of the calcium "ligninsulfonic" acid. The vanillin is purified through the sodium bisulfite compound and extraction with benzene.
4. From phenol[2] or *o*-chloro-nitro-benzene through guaiacol following the procedures and the reactions given in the flow sheet of Fig. 2. This is the usual synthetic procedure. The actual manufacturing steps are quite complicated and are carefully controlled with regard to conditions and apparatus. For these details consult the references, Schwyzer in particular.

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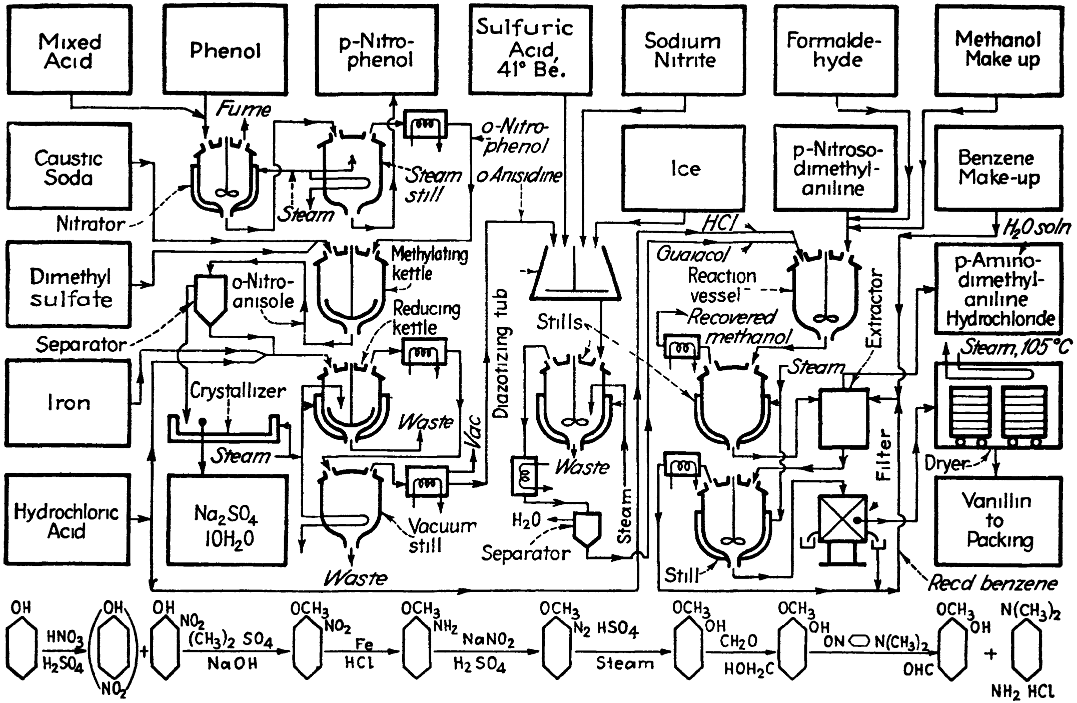
[1] Sandborn, Salvesen, and Howard, U.S. Pat., 2057117 (1936); Reissue 12268 (1936).

[2] Schwyzer, "Die Fabrikation pharmazeutischer und chemischtechnischer Produkte," pp. 205–209, 279–288, Verlag Julius Springer, Berlin; 1931; Schotz, "Synthetic Organic Chemicals," pp. 93–100, Ernest Benn, Ltd., London, 1925; Ullmann, *op. cit.*, vol. 8, pp. 815–820; Groggins, "Unit Processes in Organic Synthesis," 2d ed., pp. 48–49, 377–378, 520–521, McGraw-Hill Book Company, Inc., New York, 1938.

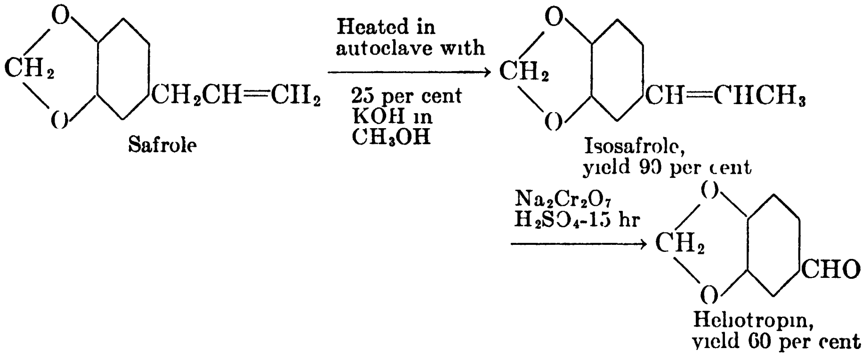


Mixed acid	1,530 lb	Hydrochloric acid	30 lb	Formaldehyde	50 lb
Phenol	400 lb	Sodium nitrite	71 lb	Benzene	30 lb
Caustic soda	750 lb	H_2SO_4, 41° Bé	280 lb	Methanol	30 lb
Dimethyl sulfate	83 lb	p-Nitrosodimethylaniline	234 lb	Direct labor	7 man-hr
Iron	25 lb			Steam	2,000 lb

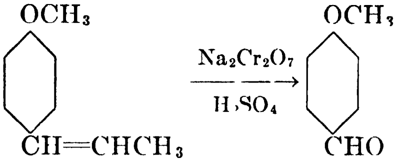
To produce 130 lb vanillin, 190 lb p-nitrophenol, and 205 lb p-aminodimethylaniline

Fig. 2 —Flow sheet for synthetic vanillin through guaiacol

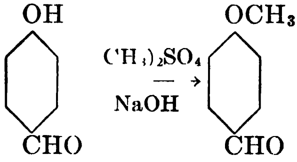
Heliotropin or *piperonal* has a pleasant aromatic odor resembling heliotrope. It is produced from safrole by the following reactions:



Anisaldehyde is a colorless oily liquid with an agreeable odor resembling coumarin which is developed only after dilution and in mixtures. It is made by the oxidation of anethole (the chief constituent of anise, star anise, and fennel oils).



p-Hydroxybenzaldehyde, as a by-product in the making of salicyl aldehyde by the Reimer-Tiemann procedure, can also be methylated to anisaldehyde.



Benzaldehyde[1] or "artificial essential oil of almond" has a burning aromatic taste and the characteristic odor of the volatile oil of bitter almond. For perfumery the product made by the alkaline hydrolysis of benzal chloride cannot be used as it contains some ring chlorination derivatives that affect the odor. Perfumery demands a "f.f.c." (free from chlorine) benzaldehyde manufactured by oxidation of toluene.

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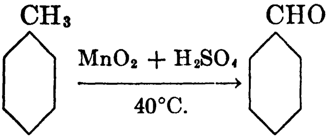
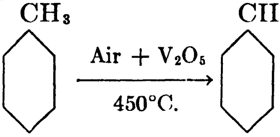
[1] GROGGINS, *op. cit.*, pp. 409–410.

Liquid phase:



$+ H_2O$

Vapor phase:



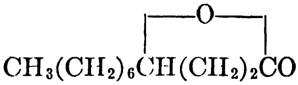
$+ H_2O; \quad \Delta H = -91,200$ cal.

MISCELLANEOUS PROCESSES

Heptaldehyde itself and in the form of its derivatives is employed in perfumery. It has a very persistent, heavy, fruity odor. Heptaldehyde, along with undecylenic acid, results from the destructive distillation of ricinoleic acid (castor oil) under reduced pressure.

$$\underset{\text{Ricinoleic acid}}{CH_3(CH_2)_5CHOHCH_2CH{=}CH(CH_2)_7COOH} \rightarrow \underset{\text{Heptaldehyde, yield 60 per cent}}{CH_3(CH_2)_4CH_2CHO}$$
$$+ \underset{\text{Undecylenic acid, yield 15 per cent}}{CH_2{=}CH(CH_2)_8COOH}$$

The gamma *lactone* of *undecylenic acid* has a peach flavor. It is known as *peach aldehyde* and is made by the action of sulfuric acid on undecylenic acid.



$$CH_2{=}CH(CH_2)_8COOH \xrightarrow{H_2SO_4} CH_3(CH_2)_6\overset{\boxed{\quad O \quad}}{CH(CH_2)_2CO}$$

Methyl heptine carbonate is an artificial violet odor. It is prepared from heptaldehyde as follows:

$$CH_3(CH_2)_4CH_2CHO \xrightarrow{PCl_5} C_6H_{13}CHCl_2 \xrightarrow{NaOH} CH_3(CH_2)_4C{\equiv}CH \xrightarrow{Na}$$
$$CH_3(CH_2)_4C{\equiv}CNa \xrightarrow{ClCOOCH_3} CH_3(CH_2)_4C{\equiv}CCOOCH_3$$

Saccharin is a powerful sweetening agent, particularly useful when a sweet flavor is desired without using a carbohydrate. It is manufactured by a series of reactions starting with toluene.[1] This is treated with chloro-sulfonic acid at 0 to 5°C. in cast-iron vessels, the following reactions[2] occurring:

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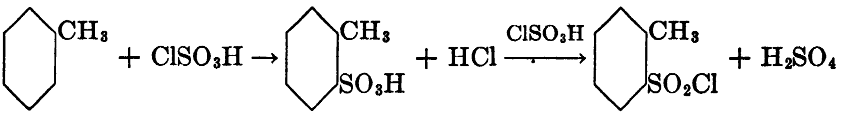
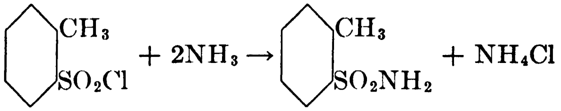
[1] Schwyzer, *op. cit.*, pp. 245–249.

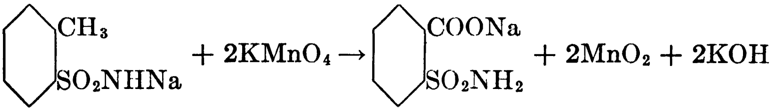
[2] Some authorities give this reaction with water splitting off and reacting with the second mole of chloro-sulfonic acid: $C_6H_5CH_3 + ClSO_3H \rightarrow C_6H_4(CH_3)SO_2Cl + H_2O$; $H_2O + ClSO_3H \rightarrow HCl + H_2SO_4$. Ullmann, *op. cit.*, vol. 2, p. 247.



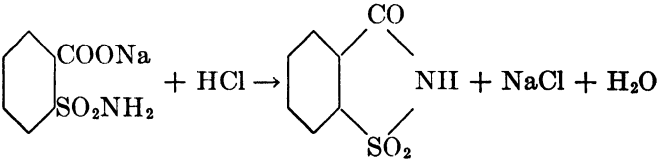
An over-all yield of 90 per cent is obtained in these reactions, the product consisting of about 60 per cent of the ortho isomer and 40 per cent of the para isomer. By pouring the products into water and freezing, the undesired para isomer is removed. The *o*-toluene sulfonyl chloride is treated with concentrated aqueous ammonia solution in enamel-lined autoclaves to give the corresponding sulfonamide in 90 per cent yield:



This product is dissolved in sodium hydroxide and oxidized with potassium permanganate.



The MnO_2 is filtered off and the solution acidified with HCl, giving the saccharin (benzosulfimide) as a precipitate.



Menthol has long been extracted as the levo- form from oil of Japanese peppermint and used in cigarettes and many other products as an antiseptic cooling flavor. The manufacture of the pure optically inactive form by the hydrogenation of thymol is now being undertaken.[1]

The *acetals* of the *aldehydes* have an odor only slightly modified from that of the aldehydes but have great alkali resistance. Hence these acetals are being used in soaps, which are very difficult to perfume with any lasting odor because the alkaline nature of the soap itself destroys any alkali sensitive product.

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[1] BARNEY and HASS, Racemic Menthol, New Synthesis from Thymol, *Ind. Eng. Chem.*, **36**, 85 (1944).

PERFUME FORMULATION

An actual example of a compound perfume, similar to a widely sold product, is given here to indicate the various components that have been discussed and to show their use in a blended product. The foundation odors are from the eugenols, methyl ionone, and the bergamot oil.

Essential oils:	
Sandalwood oil	10 g.
Bergamot oil	117 5 g.
Ylang-ylang oil	40 g.
Petitgrain oil	10 g.
Orange-flower oil	10 g.
Rose otto	15 g
Jasmine absolute	20 g
Isolates:	
Eugenol (from clove oil)	90 g
Santalol (from sandalwood)	15 g.
Semisynthetics:	
Isoeugenol (from eugenol)	110 g.
Heliotropin (from safrole)	15 g.
Methyl ionone (from citral)	237 5 g.
Synthetics:	
Coumarin ...	27 5 g.
Vanillin (from guaiacol)	20 g
Benzyl acetate	30 g
Oleoresins:	
Opopanax	2 5 g.
Balsams (resinoids):	
Tolu	5 g
Peru	7 g
Benzoin	70 g
Animal fixatives:	
Castor tincture 1:10	12 5 g
Synthetic fixatives:	
Musk ketone	32 5 g.
Musk ambrette	12 5 g
Vehicle:	
Ethyl alcohol	450 kg.

INDUSTRIAL APPLICATIONS OF PERFUMERY

Perfumes are used industrially in masking, neutralizing, and altering the odor of various products as well as in creating a distinctive aroma for normally odorless objects. "Cashmere" shawls are manufactured in Scotland and given the genuine Hindu touch by a trace of patchouli oil applied to them. Aromatics are added to fabric sizing to disguise the glue or casein smell and leave the finished product with a fine fresh smell. The correct essential oils and fixatives introduced in small quantities to paint will completely mask the usual paint odor during drying. Leather goods and paper are scented delicately to cover up the raw natural smell. A minute amount of bornyl acetate evaporated in an air-conditioning system will impart an outdoor tang to the air. The odor of kerosene in fly sprays is masked and artificial cedarwood is made by coating other woods with cedar oil reclaimed in pencil manufacturing.

The psychological effect of odors is successfully used to increase customer appeal. Perfumed merchandise outsells its odorless counterpart by a large margin. An insurance company boomed its sales of fire insurance overnight by sending out advertising blotters treated to simulate the acrid odor of a fire-gutted building. Newspapers have lately printed advertisements in ink specially mixed with a perfumed oil in order to call attention to a perfumer's product.

THE FLAVORING INDUSTRY

There are only four basic flavors which the nerve endings in the taste buds on the tongue can detect: *sweet*, *sour*, *salty*, and *bitter*. The popular conception of flavor, however, involves the combination of these four basic stimuli with the concurrent odor sensations. Apple, for instance, tastes merely sour with a trace of bitterness from the tannins present. The main concept received of an apple is due to the odor of acetaldehyde, amyl formate, amyl acetate, and other esters present in the volatile portion.

The principles of perfume blending also hold good for flavor manufacturing. The best flavoring essences are natural products altered and reinforced where necessary by synthetics. In addition to alcohol as a vehicle, glycerine and isopropyl alcohol are used for the liquid preparations with emulsions of bland gums such as tragacanth and acacia (gum arabic) for pastes. The same fixatives are employed, although the animal types are used more sparingly. Vanillin, coumarin, and heliotropin are used more liberally for this purpose.

Many of the essential oils find application in the flavor industry, the more common being the spice oils, the citrus oils, peppermint, and spearmint. Almost all the perfume synthetics find acceptance plus a number made especially for flavors. The esters of ethyl, methyl, amyl, propyl, butyl, and benzyl alcohols with acetic, propionic, butyric, salicylic, caproic, formic, valeric, and anthranilic acids are widely used to characterize the fruit flavors. As with the flower perfumes, many chemical specialties keynote individual fruit aromas. The gamma lactone of undecylenic acid is a very true representation of the fresh odor of a cut peach. A strawberry base is the ethyl ester of methylphenylglycidic acid, although it is not a true effect and partakes of a somewhat unnatural tone. Propyl succinate and ethyl butyrate are part of the make-up of many pineapple compositions.

NATURAL FRUIT CONCENTRATES

Although the essential oils used in flavoring are of the same grade and source as those used for perfumes, the fruit flavors are handled in a somewhat different manner. Owing to the large percentage of water in most of the common fruits (from 75 per cent in the banana to 90 per cent in the strawberry) and the presence of considerable amounts of sugar and other easily fermented materials, special processes must frequently be employed, such as the following:

Distillation and Extraction of the Fruit.—The ripe fruit is stoned and comminuted. It is then subjected to steam distillation and rectification until all the aroma is concentrated in a small portion of the aqueous distillate. This portion is then extracted with low-boiling petroleum ether and the ether removed under vacuum to leave an *essence* or *quintessence* of the fruit used. Cherry, apple, strawberry, and raspberry are treated by this method.

Extraction of the Juice.—In this system the expressed and filtered juice is extracted directly without previous distillation. Occasionally the juice is allowed to ferment slightly before extraction. This is supposed to result in a fuller flavor.

Concentration of the Juice.—The expressed and filtered juice is concentrated in vacuum evaporators with a low degree of heat until the water is largely driven off and the sugar concentration is high enough to inhibit bacterial growth (60 per cent). This type of concentrate often has a "jam" or cooked flavor, especially in the case of the strawberries. An alternate method of concentration is by freezing. After reducing the temperature sufficiently, the mush of practically pure water ice is filtered off, and the partly concentrated juice is refrozen and refiltered until the requisite strength is obtained. This is the optimum method of producing concentrates, as there is little injury from heat and the slight off flavors from oxidation can be avoided by running the process in an atmosphere of carbon dioxide.

Vanilla.—The vanilla bean is grown principally in Madagascar, Bourbon, and Mexico. It is the immature fruit of the orchid, *Vanilla planifolia* and is cultivated as a vine on trees which support it. The pods are picked when they are just starting to turn from a uniform green to yellow at the tip and have rather a disagreeable odor. The green pods undergo a curing treatment of from 3 to 5 months' duration. In Mexico, the beans are spread out on mats in the heat of day for an hour, after which they are packed into an insulated sweatbox to ferment for 2 days. After drying on open frames for several days, the process is repeated until the bean is cured. Variations of this method include the use of ovens in the initial step and a preliminary dipping into almost boiling water. The cured bean is pliant, shiny, and dark-colored. The odor has become full and rich, and the sweating may have left white aromatic crystals on the outside of the bean. What has happened in substance is that the glucoside, glucovanillin, present in the bean has been acted upon by a ferment and split into glucose, vanillin, and other aromatics. Substances identified in the vanilla bean are anisic acid, alcohol and aldehyde; vanillic acid and alcohol; cinnamic acid and its esters; vanillin, ethyl vanillin, and possibly other homologs of vanillin.

Preparation of Vanilla Extract.—One hundred pounds of a blend of Mexican and Bourbon beans are finely cut up and macerated cold with three successive portions of 35 per cent ethyl alcohol of 100 lb. each. These extracts are combined to make a fine vanilla extract. Other solvents may be used and the extraction carried further, but the product is coarser and less desirable as a fine flavor.

Chocolate and Cocoa.—The cacao bean, the seed of *Theobroma cacao L.*, grows on the tree in pods of from 30 to 60 beans. The tree, which when mature is about 20 ft. tall, is grown in Ecuador, Colombia, Brazil, Trinidad, and Venezuela in South America, and also on the African Gold Coast, Panama, and Mexico. The pods are gathered twice a year and are split open, and the watery pulp containing the seeds is allowed to ferment in boxes. This fermentation takes from 2 to 7 days and, in addition to liquefying the pulp, kills the embryo (115°F.), reduces the toughness of the bean, frees theobromine from the glucoside, and reduces the astringent tannin content. This fermentation is necessary for flavor in the final product. The moisture in the fermented beans, which is about 30 per cent, is reduced to 5 to 6 per cent by sun or oven drying. The bean is shipped in this condition to manufacturing centers.

The beans are heated in rotary roasters between 110 and 120°C., which develops the true chocolate flavor and aroma, removes unpleasant tannins and volatile matter (butyric and acetic acid, organic bases, and amines), dextrinizes the starch, and embrittles the husk. The roasted beans are quickly cooled to prevent overroasting, cracked in a conical mill, dehusked by a winnowing air stream, and degerminated. This product is known as *cacao nibs*.

Two common methods are used to work the cacao product into chocolate. In the first and older way, the nibs are ground on two or three buhrstone mills, sugar is added, and the mixture is transferred to a melangeur, which is a mill consisting of a revolving stone on a horizontal revolving heated bed. It merely serves to blend the coarsely ground cacao and the sugar. The paste from the melangeur is fed to a water-cooled grinder with five differentially speeded polished hard cast-iron rollers. This is a refiner and turns out a paste fine enough for conching. The newer method is to grind the sugar in a closed-circuit disintegrator and the nibs in a separate water-cooled two-stage disk mill with closed circuit removal of fines. The two are then mixed. This method takes much less power than the older one and produces a finer and more uniform product in less time. In either method, the paste is run through a concher, which is a granite bed with reciprocally acting granite rollers. It reduces the particle size to an average of less than 1 micron. It is steam-heated to run at 160°F. or can be allowed to heat itself by friction (122°F.). There is a further loss of unpleasant volatile material at this point and the full flavor and body of the chocolate are developed here by the heat and interaction of the cacao and the sugar. Milk chocolates are prepared by adding condensed fresh milk or milk powder to the melangeur. The finished product has a cocoa butter content of 30 to 35 per cent and not less than 12 per cent of milk solids.

For cocoa, the roasted and ground beans are subjected to pressure in hydraulic presses to remove some of the fat content. Whereas originally roasted beans contain 55 per cent of fat, the product remaining after this treatment has the fat reduced to 20 per cent and is known as *cocoa.* The removal of fat makes a beverage that is not too rich and one in which the fat does not separate on top. Some cocoa is treated in between the first and second pressings with 5 per cent of potassium, sodium, or ammonium carbonate. This darkens the cocoa and is supposed to make a more soluble product. Cocoa so treated is known as *Dutch-process* cocoa.

FLAVOR ESSENCE FORMULATION

A formula is given here for a type of apricot flavoring to be used in candy manufacture. This will indicate in general how a well-balanced flavor is made up of natural products reinforced with suitable synthetics. Many formulas are to be found in print which consist mainly of esters of synthetic origin. These are harsh and unnatural and in many cases the only resemblance to the original is in the designation of the flavor.

APRICOT ESSENCE

	Grams
Apricot extract (a natural product)	1,000
Gamma lactone of undecylenic acid (persicol)	10
Nonyl aldehyde (apricolin)	1
Vanillin	0.5
Ethyl vanillin (bourbonal)	0.2
Ethyl cinnamate	0.2
Benzyl cinnamate	0.2
Tannic acid	0.1

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CHAPTER XXVIII

OILS, FATS, WAXES

There are, at present, about 10 billion pounds of animal and vegetable fats and oils consumed in the United States each year, of which 85 per cent are of domestic production and 15 per cent imported. Figure 1 depicts the relative consumption for food, soap, and paint of the various oils and

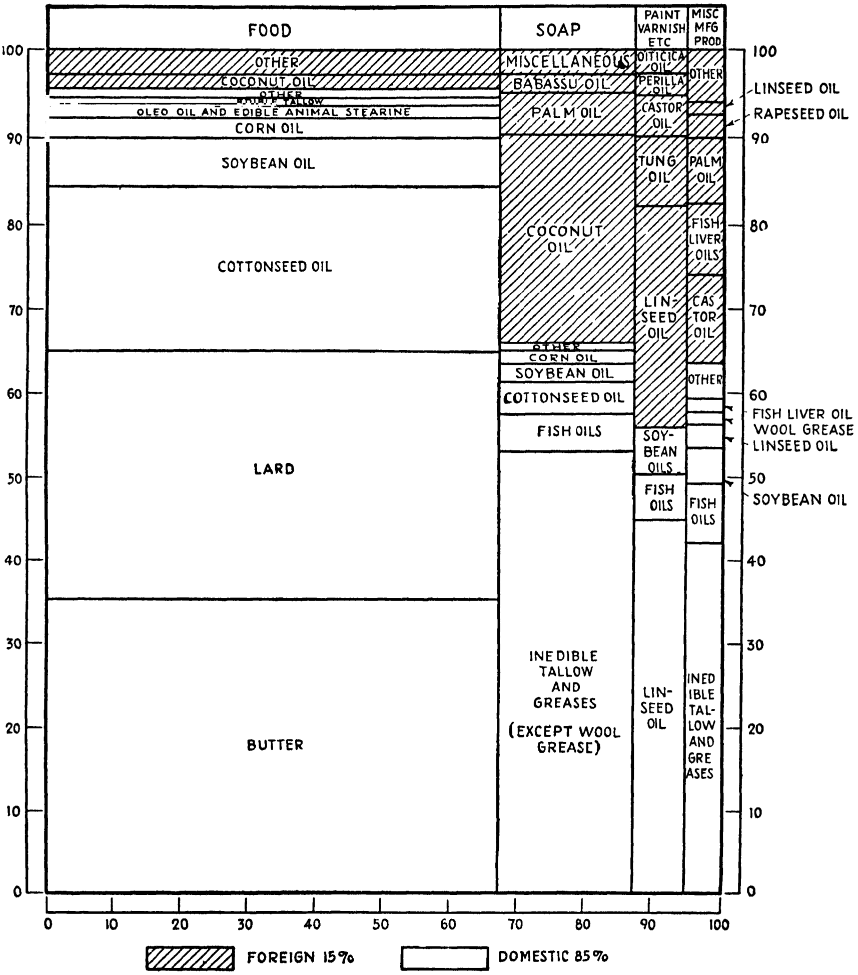

Fig. 1.—Fats and oils, 1940.

fats. It also shows the direct competition of the chemical industries of soap and paint manufacture with basic food products. Fats and oils are found widely distributed in nature, in both the plant and the animal kingdoms. Waxes, likewise, are natural products but differ slightly from the fats and oils in their basic composition. Whereas the fats and oils are mixtures of the glycerides of various fatty acids, the waxes are mixed esters of mono- and dihydric alcohols, with fatty acids.

TABLE 1.—FATTY ACID CONTENT OF VARIOUS OILS AND FATS[a]
(The figures under the various oils express per cent present)

No. of C atoms	Acid	Formula	Cotton-seed oil	Soy-bean oil	Corn oil	Men-haden oil	Whale oil	Mutton tallow	Coconut oil
6	Caproic	$C_5H_{11}COOH$	....	....	....	....	....	....	Trace
8	Caprylic	$C_7H_{15}COOH$	....	....	....	....	....	....	7.9
10	Capric	$C_9H_{19}COOH$	....	....	....	....	....	....	7.2
12	Lauric	$C_{11}H_{23}COOH$	....	....	....	....	....	....	48.0
14	Myristic	$C_{13}H_{27}COOH$	0.5	....	....	9.2	4.5	4.6	17.5
16	Palmitic	$C_{15}H_{31}COOH$	20.9	6.5	7.3	22.7	11.5	24.7	9.0
16	Unsaturated	$C_{15}H_{29}COOH$	..	....	....	....	17.0		
18	Stearic	$C_{17}H_{35}COOH$	1.8	4.2	3.3	1.8	2.5	30.4	2.1
18	Oleic	$C_{17}H_{33}COOH$	29.2	32.0	43.4	....	....	36.0	5.7
18	Linoleic	$C_{17}H_{31}COOH$	42.8	49.3	39.1	....	....	4.3	2.6
18	Linolenic	$C_{17}H_{29}COOH$	....	2.2					
18	Unsaturated	....	....	....	....	24.9	36.5		
20	Arachidic	$C_{19}H_{39}COOH$	0.1	0.7	0.4				
20	Unsaturated	....	....	....	....	22.2	16.0		
22	Unsaturated	....	....	....	....	20.2	10.0		
24	Lignoceric	$C_{23}H_{47}COOH$	....	0.1	0.2				
24	Unsaturated	....	....	....	....	....	1.5		

[a] GUILLAUDEU, Industrial Utilization of Fats and Oils, *Ind. Eng. Chem.*, **31**, 158 (1939).

Table 1 indicates the characteristic composition of various important oils in regard to their fatty acid content. These acids fall within (1) the saturated series as exemplified by stearic acid and are the basis for the nondrying oils, (2) monoolefinic series with one double bond between carbons as illustrated by oleic acid, and (3) polyolefinic series with more than one such double bond as exemplified by linoleic and linolenic acids. The latter two classes of acids, being unsaturated, furnish the semidrying and drying oils, according to the amounts of unsaturation present. It is of interest to note that the chief constituents of the vegetable oils are the

16 and 18 carbon acids, while the 20, 22, and 24 carbon acids predominate in the fish oils. Coconut oil is unique in that it consists of esters of much shorter carbon chain acids, the 12 and 14 carbon acids being present in greatest amounts. Most oils contain a number of different fatty acids, from 6 to 10.

The degree of unsaturation of the acids involved affects the melting point of the ester mixture, the more unsaturated acids giving esters with lower melting points, these being the chief constituents of the oils. The more saturated esters, on the other hand, are constituents of the fats. Thus, we see that the factor determining whether one of these compounds is termed a *fat* or an *oil* is merely its melting point. These oils are called *fixed oils* in distinction from the essential or *volatile* oils described in Chap. XXVII. The fixed oils cannot be distilled without some decomposition under ordinary atmospheric pressure. Differentiation should also be noted from petroleum oils discussed in Chap. XXXVII.

Historical.—Since ancient times man has known how to remove oils and fats from their natural sources and fit them to his own uses. The animal fats were first consumed as food, but it was not long before the burning of the oils for light and heat was learned. The obtaining of oils from vegetable sources is of ancient origin, for the natives in the tropical regions of the globe have long been removing these oils from various nuts after drying them in the sun. The utilization of marine oils began with the whaling industry, which was started by the Basques in the Bay of Biscay in the fifteenth century. This industry has been greatly expanded and modernized through the years.

The first chemical reaction applied to fats and oils (excluding oxidation in burning) was that of saponification to give soap. The early raw materials were mainly of animal origin, the rendering of animal flesh being an old art.

Industrialization of oils and fats began with the erection of a cottonseed mill in South Carolina about 1826. The methods were crude and the product impure. The industry did not expand very rapidly until after 1865. In 1850, the use of caustic soda to remove free acids from the oil was introduced from France. About this time, the millers became aware of the value of the linters that clung to the hulls and also of the hulls themselves for cattle feed. By 1887 more scientific methods of refining had been introduced.

The beginning of the oleomargarine industry in Chicago in 1885 gave a large impetus to the cottonseed oil industry, since it was found that the oil could be used as a thinning agent in oleomargarine. The higher quality demanded by this new market produced several processing improvements. Fuller's earth was used to decolorize the oil. In 1893 it was learned that the oil could be deodorized by blowing steam through it at high temperatures. Later it was found that deodorization under reduced pressure bettered both flavor and odor.

In 1900 the discovery that oils could be hydrogenated to produce fats revolutionized the entire oil and fat industry and led to our modern hydrogenated shortenings. This discovery also made marketable many of the lesser known oils, which up to that time had not been usable. This phase of the industry has advanced rapidly, until today there are 1,410,000,000 lb. of shortening and 917,000,000 lb. of hydrogenated oils produced[1] in the United States each year.

Uses and Economics.—The fats and oils have always had an essential role as food for mankind. In addition, however, our modern industrial world has found many important applications for them. The uses are summarized in Fig. 1. The oils are saponified, hydrogenated, and sulfonated to a great number of usable products.

There are two broad classifications for the fats and oils: edible[2] and inedible. The consumption of fats and oils in *edible* products represents about 67 per cent of all uses of these materials. The various edible oils, cottonseed, olive, soybean, corn, etc., are employed for salad dressings, other table uses, and for cooking purposes. The hydrogenated fats for cooking and baking, such as Crisco and Spry, may include a wide variety of vegetable oils, such as cottonseed, peanut, and soybean, since the hydrogenating process removes the color, flavor, and odor of the original source. The various fish-liver oils are used in the medicinal field for their vitamin content. Castor oil is a well-known cathartic.

In 1940 about 33 per cent of all oils and fats consumed in the United States were for *inedible* purposes, as shown by Fig. 1. Almost two thirds of these inedible oils were used in the soap industry. These include ~~tallow,~~ coconut oil, palm oil, and certain greases. Others were slightly hydrogenated to make them suitable for soapmaking.

The drying oil industries (including paints and varnishes) consume one fifth of all inedible oils. The major oil is still linseed, with tung, perilla, fish oils, soybean, and castor in minor demand. These drying oils are all essentially unsaturated and produce films or coatings upon drying. They are also employed with synthetic resins and cellulose derivatives to give special types of films. Castor oil, linseed, soybean, rapeseed, and cottonseed oils are being used to some extent as plasticizers for nitro-cellulose lacquers.

The miscellaneous industries consuming these inedible fats and oils include the oilcloth and linoleum industry, the printing industry, the tin-plate industry, ~~and~~ the manufacture of Artgum, the well-known artificial eraser and cleaner. Castor oil is an ingredient of hydraulic brake fluids, tallow is a constituent of marking crayons, and a wide variety of the oils form an integral part of various polishes, creams, and emulsions. Lard oil is used for certain illuminating purposes, owing to its penetrating power in fogs.[1] Large quantities of sulfonated glycerides serve as wetting agents and detergents, especially in the textile industry;

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[1] ANON., Fats and Oils, *Chem. & Met. Eng.*, **49**, No. 2, 98 (1942); ANON., Oils and Fats, *Chem. & Met. Eng.*, **47**, 87 (1940).

[2] VAHLTEICH, Custom Built Fats, *Chem. Eng. News*, **21**, 1238 (1943).

TABLE 2.—PRODUCTION IN POUNDS OF FATS, OILS, AND DERIVATIVES IN 1941[a]

	Millions of Pounds
Animal:	
Butter	1,900
Lard	2,200
Tallow (edible)	91
Tallow (inedible)	1,512
Stearin (edible)	48
Neat's-foot oil	4
Whale oil	2
Vegetable:	
Corn oil	204
Cottonseed oil	1,395
Coconut oil	573
Soybean oil	587
Linseed oil	741
China wood (tung) oil	26
Peanut oil	152
Babassu oil	36
Castor oil	131
Palm oil	223
Perilla oil	5
Rape oil	16
Sesame oil	3
Teaseed oil	1
Olive oil (edible)	18
Olive oil (inedible)	5
Oiticica oil	30
Fish:	
Cod-liver oil	9
Other fish oils	198
Derivatives:	
Shortening	1,410
Hydrogenated oils	917
Lard oil	51
Tallow oil	11
Fatty acids	160
Red oil	77
Stearin—vegetable	86
Stearin—animal	40

[a] Based on *Chem. & Met. Eng.*, **49**, 98–102 (1942).

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[1] LEVITT, Industrial Uses of Animal Oils, *Chem. Industries*, **42**, 419 (1938).

here also should be included the sulfated fatty alcohols and derivatives (see Chap. XXIX).

Table 2 details the statistics[1] of the principal fats and oils together with their important derivatives. This tabulation includes both the edible and the inedible divisions. It should be compared with Fig. 1. The total production in 1941 was 10,264,000,000 lb. derived from 8,900,000,000 lb. produced domestically and 1,364,000,000 lb. imported. Domestic production of soybean oil is very much on the increase, occasioned by enlarged cultivation of soybeans.

The *waxes*,[2] carnauba, beeswax, and sperm wax, enter into the manufacture of various polishes for floors, shoes, automobiles, and furniture. Other outlets include the making of carbon paper, candles, electrical insulation, waterproof textiles, and phonograph records.

VEGETABLE OILS

For purposes of discussion of the various technical aspects, the three classical divisions of the general subject of oils, fats, and waxes will be retained: vegetable oils, animal oils and fats, and waxes. Under each

TABLE 3.—APPROXIMATE OIL YIELDS OF CERTAIN VEGETABLE OIL MATERIALS[a]

Raw Material	Oil Yield, Per Cent
Babassu kernels	63
Castor beans	45
Corn kernels	4.5
Copra	63
Cottonseed	15.5
Flaxseed	34
Hempseed	24
Kapok seed	18
Palm kernels	45
Peanuts in the shell	25–30
Peanuts shelled	40–50
Perilla seed	37
Rapeseed	35
Sesame seed	47
Soybeans	15
Tung nuts	50–55

[a] Mostly taken from U.S. Tariff Commission, "Fats, Oils, and Oil-bearing Materials in the U.S.," Washington, Dec. 15, 1941.

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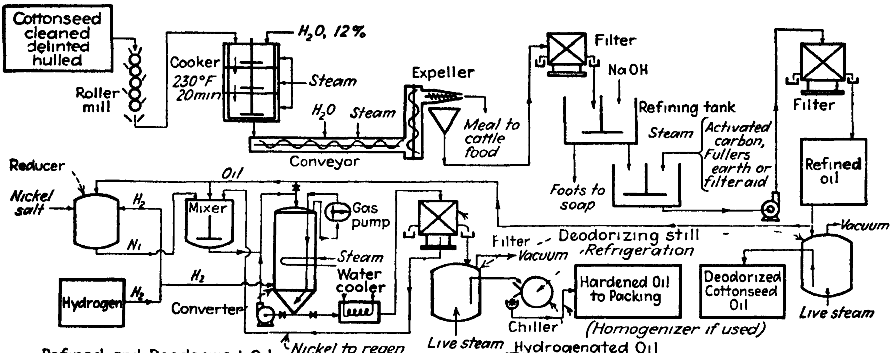
[1] Statistics of these industries are available from *Chemical & Metallurgical Engineering* in their various statistical issues, but the U.S. Tariff Commission has published the following very excellent summary of such data: "Fats, Oils, and Oil-bearing Materials in the U.S.," Washington, Dec. 15, 1941; see also Murphy, The American Balance Sheet in Oils and Fats, *Chem. Industries*, **50**, 476–485, 618–626, 768–777 (1942).

[2] MELLAN, Waxes—Animal, Mineral, Vegetable, Synthetic, *Chem. Industries*, **37**, 593 (1935).

of these headings the general methods of manufacture will be discussed, after which the most important of the individual members will be presented. Table 3 indicates the yields of vegetable oils from some of the usual sources.

The two general methods employed in obtaining vegetable fats and oils are expression and solvent extraction. The first of ~~these is~~ by far the more widely used in the United States. Solvent extraction is practiced by a few plants for certain specialized purposes, but the process as a whole is much more common in Europe.



Refined and Deodorized Oil

Cottonseed	55 lb	Per gallon oil
NaOH	01 lb	
Water (*cooling*)	20 gal	
Steam	15 lb	
Direct labor	0015 man hr	

Hydrogenated Oil

Refined cottonseed oil	0 134 gal	Per pound hardened oil
Nickel	0 00075 lb	
Hydrogen	075 cu ft	
Water (*cooling*)	06 gal	
Steam	05 lb	
Direct labor	0 0006 man hr	

Note *This flow sheet combines processes not ordinarily performed in the same plant The first processor may produce crude oil, for example, while a second will refine and hydrogenate it Oils hydrogenated for food are deodorized after hardening*

FIG. 2.—Flow sheet for cottonseed oil, refined and hydrogenated

Manufacturing Cottonseed Oil by the Expression Process.—The obtaining of crude vegetable and animal oils involves almost altogether only the *physical* changes or unit operations, but the *chemical* changes or unit processes are concerned in the refining and the hydrogenation of such oils. Figure 2 presents flow sheets for crude, refined, and hydrogenated cottonseed oils. The flow sheet for crude oil can be broken down into the following sequences of *unit operations* (Op.) (hydrogenation will be considered under its own special heading):

The cottonseeds are cleaned, delinted, and dehulled (Op.).

The kernels are then rolled or ground to prepare them for expression of the oil (Op.).

Two methods of expression are in common use: that of a hydraulic press (Fig. 3) and the expeller (Fig. 4). The hydraulic press is employed to express the oil from cooked meal. The expeller operates on uncooked meal and produces the so-called *cold-pressed* oils. If the press is used, the ground meal is cooked with steam for from ½ to 1½ hr. (Op. and Pr.). The cooked meal is formed into cakes and placed in the hydraulic press. The pressure applied at the start of the operation is about 500 lb. per sq. in., but as the oil starts to flow the pressure is increased gradually to a maximum of 5,000 lb. per sq. in. (Op.).

The press cakes are often re-pressed at higher temperatures to obtain additional oil of somewhat lower quality. The cakes, which contain 6 to 10 per cent oil, are broken, ground, and used for cattle feed (Op.). The Anderson expeller is a horizontal chilled cylinder equipped with worms of progressively smaller pitch on a single shaft. The uncooked meal is carried along the cylinder by the worms toward the restricted opening at the far end. A pressure of approximately 12,000 lb. per sq. in. is developed and the oil is forced out through openings between the bars (Op.). The residual meal contains only 4 to 5 per cent oil.

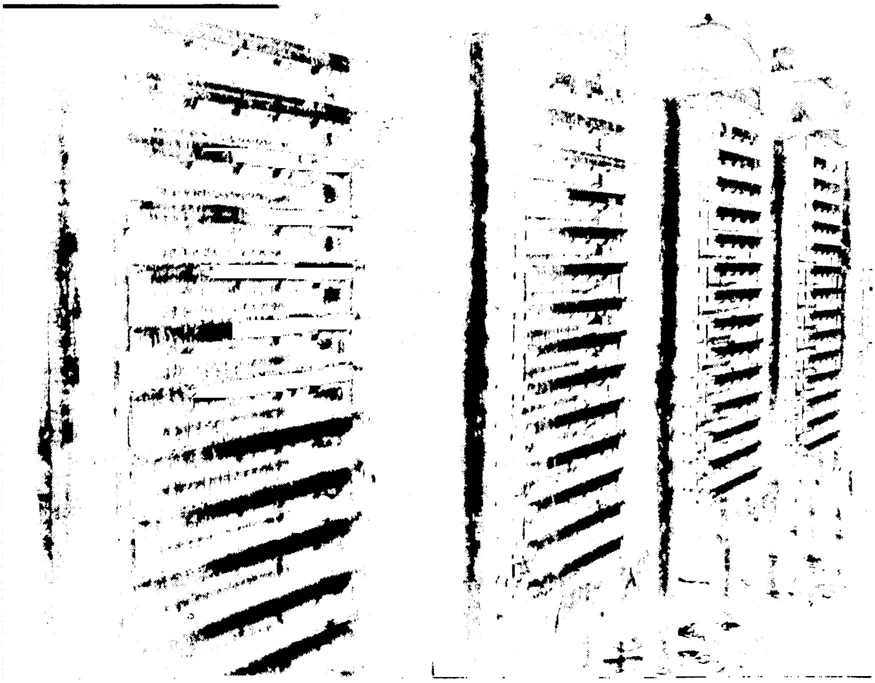


Fig. 3.—Hydraulic press removing oil from cottonseed. (*Courtesy of National Cottonseed Products Association.*)

It should be noted that cold pressed oils are of the highest quality and are frequently used for food purposes.

The yields attained from 1 ton of crude cottonseeds average: oil, 300 lb.; cake, 1,000 lb.; hulls, 500 lb.; linters, 100 lb.; loss (chiefly moisture), 100 lb. Altogether, cottonseed oil is our most valuable vegetable oil and has been made so largely by the contributions of chemistry and engineering.[1]

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[1] Holcomb, Chemistry's Contribution to the Cottonseed Industry, ***Chem. Eng. News*, 20,** 438 (1942); Wesson, Progress in Vegetable Oil Production, ***Am. Inst. Chem. Engrs. Silver Anniv. Vol.*** (1935).

Manufacturing by Solvent Extraction.—The second general method of obtaining the crude vegetable oils is by solvent extraction[1] and is employed in the United States for specialized purposes; *e.g.*, to obtain proteins from the meal, to remove *all* oil from the cake so that it may be used for plastics, or to recover the vegetable phosphatide, lecithin. This latter is valuable in the rubber and leather industries and to the food industry as an antioxidant (see Fig. 5).

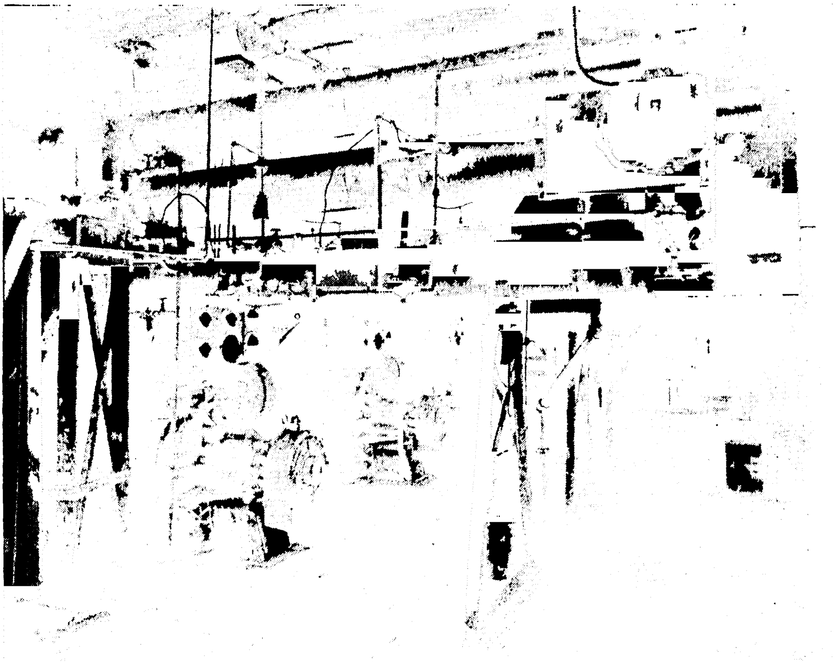

Fig. 4.—Expeller pressing oil out of cottonseed. (*Courtesy of National Cottonseed Products Association.*)

A considerable amount of soybean oil is solvent extracted, for which a number of solvents are employed, some of the more important ones being acetone, benzene, gasoline, carbon disulfide, and the various chlorinated solvents. The raw products to be extracted are not ground so fine as in expression process. The equipment[2] consists of agitated extractors connected so that countercurrent operation may be carried out. After the solvent has become saturated with oil, it is taken to a stripping column where the oil and solvent are separated. The spent cake from the diffusion battery is given a steam distillation to recover any remaining solvent and is then generally ~~dried and sold for~~ cattle food.

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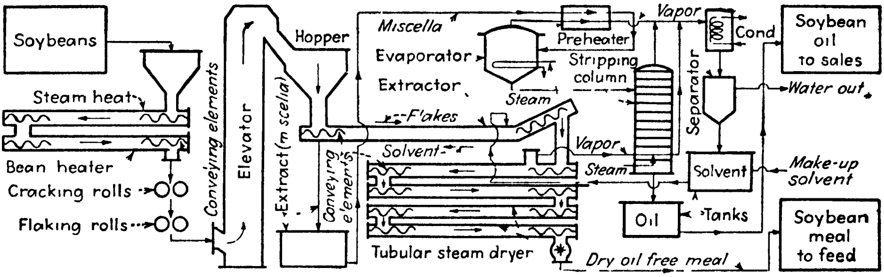
[1] Goss, Modern Practice in Solvent Extraction, *Chem. & Met. Eng.*, **48,** No. 4, 80 (1941). There the three methods of obtaining an oil are compared.

[2] Soybean Extraction with Normal Hexane, *Chem. & Met. Eng.*, **48,** No. 9, 128 (1941), pictured flow sheet.

Crude oils, obtained by either of the processes outlined above, should be subjected to a *purification* or *refining* treatment (see Fig. 2). The first step in such refining consists in removing the free fatty acids present by neutralization with caustic soda, forming soaps. These soaps, commonly called *foots,* are removed by means of centrifuges or filters. Time, temperature, and the degree of agitation during neutralization are chosen according to the properties of the oil being treated.

The second step is *bleaching,*[1] which is accomplished with a mixture of activated carbon and fuller's earth, at about 230°F. under atmospheric pressure, or as low as 65°F. under vacuum. The mixture is stirred about a half hour and then filtered through a plate-and-frame press. The resulting oil should be kept out of contact with air to reduce the tendency to darken once more.



Soybeans	5 56 tons	To produce 1 ton oil and 4 56 ton oil free meal in a plant treating 10 tons beans per day
Trichlorethylene loss	3 17 gal	
Coal	1 61 ton	
Labor per shift	1 man	

FIG. 5.—Soybean oil extraction—Detrex process.

The last step is usually *deodorization,* which is effected by blowing superheated steam through the oil in a vacuum of about 29.5 in. mercury. The ~~highly volatile~~ substances are steam-distilled off. The deodorized oil is clarified and polished by filtration.

Some oils must be subjected to a *winterizing* treatment, which consists of cooling the oil to a low temperature by refrigeration, adding filter aid, and filtering off the waxes that crystallize out. Other special treatments are given oils to prepare them for specific use in the paint, enamel, and varnish industry. Blown oil is made by passing air through the oil at 120°F. in the presence of cobalt acetate, until the resulting increase in viscosity has reached the desired point. Stand oil is the product resulting from the heating of the oil in covered varnish kettles, at 425°F. (260°C.) until the desired viscosity has been obtained.

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[1] PERRY, *op. cit.*, p. 1308.

Linseed Oil.—The flaxseed produced in this country is grown largely in North and South Dakota, Minnesota, and Montana. The production and refining are carried out similarly to that for cottonseed oil depicted in Fig. 2, either hydraulic presses or Anderson expellers being employed. The average oil content of the flaxseed is about 40 per cent, which would indicate a yield of about 34 per cent on the weight of the seeds, leaving about 6 per cent oil in the press cake.

Soybean Oil.—Soybeans[1] have been an important crop in this country since 1880 and are grown largely in the cotton belt and the lower corn belt. The principal mills are in Illinois, Iowa, and Indiana. Although most of the domestic oil produced is obtained by the expression method, the Ford Motor Company and others employ the solvent extraction method. Ford uses the oil as the modifier in enamel and employs the cake in the resin as the basis of the enamel. Table 3 indicates that soybeans yield an average oil content of 15 per cent and, in addition, contain lecithin. An average yield from 1 ton of soybeans is about 250 lb. of oil and 1,600 lb. of cake. The cake will contain about 45 per cent protein material and is used not only as cattle food but also as human food.

Coconut Oil.—The raw material for the production of coconut oil[2] is all imported from various tropical countries, a large part coming from the Philippines, because of the freedom from duties and excise taxes. The raw material is brought in as copra, which is coconut kernel that has been shelled, cut up, and sun-dried at the point where grown. This treatment not only avoids the cost of shipping excess moisture but also prevents deterioration of the oil. The coconuts, as they come from the tree, contain from 30 to 40 per cent oil, while the copra contains from 60 to 65 per cent oil. The oil is extracted in two pressings: the first in an Anderson expeller, the resulting cake being sent to hydraulic presses. Here it is re-pressed, at 4,000 to 5,000 lb. per sq. in. The combined oils are refined. Refined coconut oil and coconut stearin are used chiefly in the manufacture of vegetable margarines and soaps. The highest grade oil is snow white and almost neutral.

Corn Oil.—The production of corn oil differs from some of the others in certain respects. After cleaning, the corn is placed in large tanks and steeped with warm water containing SO_2, thus loosening the hull from the kernel. The steeped corn is run through the "attrition" mills, which break the germ away from the rest of the kernel. The separation of the germ and the kernel is accomplished by running the mixture into a tank of water, where the germ floats, owing to its oil content, and is skimmed

[1] HAUSMAN, Soybean Oil, *Soap*, **12**, No. 12, pp. 27–30, 39, 77, (1936); BILBE, What Soybean Processing Costs, *Chem. & Met. Eng.*, **48**, 85 (1941).

[2] HAUSMAN, Coconut Oil, *Soap*, **11**, No. 9, 23 (1935).

off. Before going into the ordinary grinding and expelling apparatus, the germ should be washed and thoroughly dried. The crude oil from the expellers (see Fig. 4) is given the usual purification treatment, such as that described under Cottonseed Oil. The oil content of the corn kernel, exclusive of the hull, is about 4.5 per cent. Corn oil is one of those which must be hydrogenated before it can be used in soapmaking. This oil enters extensively in foods as a salad oil.[1]

Palm Oil.—Palm oil[2] is prepared from the fruit of the palm tree, which has been cultivated on plantations in the Dutch East Indies, the Malay Peninsula, and elsewhere. The palms grow naturally on the west coast of Africa. The fruit is 1 to 2 in. long, oval-shaped, and weighs, on an average, about 6 to 8 grams. The oil content ranges from 30 to 70 per cent of the kernel or seed. The oil is obtained in two separate procedures. In the first, the oil is removed from the fruit and in the second from the kernels, or seeds. The former is done at the place where the fruit is grown. The procedure consists in cooking the fruit in large steam-pressure digesters equipped with agitators. From the steaming, the charge goes to basket centrifuges, where a 10-min. treatment, accompanied by blowing with live steam, separates the oil. The residual fiber and kernels are dried in a rotary continuous drier and separated by a screening operation. The nuts or kernels are bagged and shipped to the United States, where they are processed by the previously described methods for oil removal. The fibers are burned under the boilers of the first processing plant. About 80 per cent of the consumption of this oil in the United States goes into soap manufacture.

Peanut Oil.—Peanut oil[3] is produced by either the hydraulic press or the Anderson expeller, from the peanuts grown in the various Southern states, especially Virginia. The yield from 1 ton of shelled peanuts is about 600 lb. of oil and 800 lb. of cake. The oil is hydrogenated and refined for use in the manufacture of vegetable margarines, salad and cooking oils, and in some vegetable shortenings. Inedible grades of the oil are consumed by the soapmaker. Owing to the demands for the nuts for other purposes also (salted nuts, candy, peanut butter), large quantities of peanuts and peanut oil are imported.

Tung Oil.—Tung or China wood oil[4] is obtained from the fruit of the tung tree which grows extensively in China. Since 1923 large-scale planting has been carried out in Florida and has become one of the prime industries of that state. Owing to the war, the imports in 1941 fell from about 70,000,000 to 26,000,000 lb. The oil is obtained by use of the Anderson expeller (Fig. 4) which removes all but about 5 per cent of the 50 to 60 per cent oil content of the original nut. The oil obtained has a light straw color and requires no refining other than settling or filter pressing. It is chiefly consumed in the manufacture of varnishes, floor and wall paints, oil cloth, linoleum, and enamels. The cake is used as fertilizer because of its high nitrogen and phosphorus content.

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[1] Durkee, Making Salad Oil from Corn, *Food Industries*, **3**, 251 (1931).

[2] Hausman, Palm Oils, *Soap*, **12**, No. 2, 26 (1936).

[3] Lynch, Peanut Oil, *J. Chem. Education*, **7**, 1617 (1930).

[4] Beisler, Some Chemical Problems of the Florida Tung Oil Industry, *J. Chem. Education*, **7**, 2344 (1930); Beisler, Recovering Tung Oil from Nuts Grown in Florida, *Chem. & Met. Eng.*, **37**, 614 (1930).

Babassu Oil.—This oil[1] is expressed from the kernels of the fruit of the palm *Orbignya speciosa*, which grows in Brazil. The kernels contain 63 to 70 per cent of an oil resembling coconut oil. They are very difficult to remove from the nut itself because of the hard, thick shells. The oil is employed in Europe for soaps, as well as for edible purposes. The press cake is suitable for stock feed, containing 20 to 23 per cent protein.

Perilla Oil.—This is a deep yellow or greenish oil, similar to linseed oil. It is yielded by the seeds of the *Perilla ocymoides*, which resemble mustard seeds. It is consumed for both edible and technical purposes. The latter include the waterproofing of paper, making cheap lacquers and varnishes, and the manufacture of linoleum.

Castor Oil.—This well-known oil is obtained from the seeds or beans of the castor plant found in most tropical regions. The beans contain 35 to 55 per cent oil and are expressed or solvent-extracted. The finest grade of oil is reserved for medicinal purposes. The lower grades are used in the manufacture of transparent soaps, flypaper, typewriter inks, and as a motor lubricant. Large quantities of the oil are sulfonated to produce the familiar Turkey-red oil long employed in dyeing cotton fabrics, particularly with alizarin. In the past few years, out of castor oil has been manufactured a drying oil by chemical treatment as described in Chap. XXIV on paints. This manufactured product compares very favorably with tung oil previously imported.

Oiticica Oil.—Oiticica oil is obtained from the seeds of the South American oiticica tree. It is an excellent drying oil and is used in the paint and varnish industries as a partial replacement for tung oil.

ANIMAL FATS AND OILS

There is no particular method common to the manufacture of all animal oils and fats.

Lard and Lard Oil.—Lard is produced by the rendering of hog fat and is used for food. Lard oil is the most important of the animal oils and is expressed from "white grease," an inedible lard. The white grease is prepared by a circulating rendering process such as that of Wurster and

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[1] JAMIESON, "Vegetable Fats and Oils," Reinhold Publishing Corporation, New York, 1932.

Sanger,[1] wherein the ground fat is rendered or sharply separated into the lard or pure fat, and the nonfat or cracklings. This circulating process involves a low-temperature heating under circulation and a vacuum wherein the lard is removed as a liquid fat more quickly than usually, thus avoiding its yellowing. The white grease is seeded with stearin and held at 50°F. to allow the stearin to crystallize out (graining). After the graining process is completed, the grease is wrapped in duck, stacked in a hydraulic press, and expressed. The oil is used for illumination and in the textile industry. The stearin is employed for the manufacture of soap.[2]

Neat's-foot Oil.—The skin, bones, and feet of cattle (exclusive of the hoofs) are cooked in water for 10 hr. to separate the fat. This is skimmed off the top of the water and, after filtering through cloth, heated in a kettle to 250°F. for several hours. The kettle is cooled, the contents are settled, the oil is drawn off, filtered through flannel bags, and sent to the refinery. Here the oil is "grained" in the manner described above for lard oil. This requires about two weeks at 34°F. The product is pressed once, yielding pure neat's-foot oil. The stearin from the first pressing is re-pressed to yield a second grade of oil. The pure variety is used for oiling watches and other fine machinery, the latter in the textile and leather industries. The stearin from the second pressing is consumed in soap.

Whale Oil.—This oil is now obtained from modern floating factory ships which catch, butcher, and process the mammals at the scene of the catch. To prepare the oil, the blubber is stripped from the flesh and boiled in open digesters. The finest grade of oil separates first. It is practically odorless, very pale in color, and contains very little free fatty acids. Upon continued boiling a second grade is obtained and, if the residue from this operation is cooked under pressure, a third grade is made available. All grades are centrifuged further to clarify and dry them before being placed in storage. The oils obtained are used in the manufacture of oleomargarines and lard substitutes and in soapmaking.[3] Both fish and whale oils contain unsaturated fatty acids of 14 to 22 carbon atoms, and as many as 6 double bonds.

Cod-liver Oil.—This oil, whose value was known long before the discovery of vitamins, was originally prepared by storing the fish in barrels and allowing them to rot until the oil floated to the top. It is now manufactured by live steam cooking of the livers (and other parts) of the cod and halibut, until a white scum floats to the top. This usually requires about 30 min., after which the mass is settled for 5 min., decanted, and strained. The oil desired for medicinal purposes is filtered, bleached, and wintered. It is rich in vitamins A and D.

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[1] Circulars, Wurster & Sanger, Inc., Chicago, Ill.

[2] LEVITT, Industrial Uses of Animal Oils, *Chem. Industries*, **42**, 419 (1938).

[3] RADCLIFFE, The Whaling Industry, *Ind. Eng. Chem.*, **25**, 764 (1933).

Shark-liver Oil.—Recent investigations have shown that the oil obtained from the liver of the shark, *Galeorhinus zyopterus*, contains more vitamins A and D than cod- or halibut-liver oils. It is rapidly becoming the most important of the fish-liver oils for use in supplying these two vitamins.

Fish Oils.—Fresh menhaden, sardine, and salmon are cooked whole by steam for a short period and pressed. The oil is settled (or centrifuged[1]) and wintered. The remainder of the fish is dried, pulverized, and sold as meal for feed. Each fish contains, on the average, 20 per cent oil by weight.[2] The oils are consumed in paints, as lubricants, in leather and soft-soap manufacture, and sulfonated to give a variety of Turkey-red oil.

The tremendous quantities (Fig. 1) of *butter* and *tallow* produced for food in the United States might logically warrant discussing with the other animal oils. Their methods of processing, however, are fairly well known.

WAXES

There are animal, vegetable, mineral, and synthetic waxes, depending upon their source. The animal waxes are secreted as protective coatings by certain insects. The vegetable waxes are found as coatings on leaves, stems, flowers, and seeds. The mineral waxes are the paraffin waxes obtained from petroleum and such waxes as are yielded by coal, peat, and lignite. The mineral waxes from petroleum are not true waxes (esters) but are so classified because of their physical characteristics.

Beeswax.—This is probably the best-known wax. It is made from the honeycomb by solvent extraction, expression, or by boiling in water.

Carnauba Wax.—This wax[3] is obtained from the carnauba palm which grows in Brazil. The leaves are cut, dried for 3 days, and sent to the beater house. The drying loosens the wax which can be easily beaten from the slashed leaf and falls to the floor, where it is gathered at the end of the day and melted. One gallon of powdered wax yields about 1 qt. of molten wax. This is filtered hot through cheesecloth, allowed to harden, and sold. Five palm trees will produce about 1 lb. of wax per year. The product is used as a constituent of floor, automobile, and furniture polishes, in carbon paper, candles, and certain molded products.

Sperm Oil.—The oil removed from the head cavity and parts of the blubber of the sperm whale is in reality a wax, owing to its chemical composition. By chilling this oil at 32°F. for several weeks, a solid wax called *spermaceti* settles out. This constitutes about 11 per cent of the original oil and is largely cetyl palmitate.[1] It is melted, treated with hot, dilute caustic soda solution, washed with water, and run into molds to solidify. It is translucent, odorless, and tasteless and is used in candles and ointments.

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[1] SMITH, Advances in Menhaden Production, *Chem. & Met. Eng.*, **47**, 99 (1940).

[2] LANGTON, Fish and Marine Animal Oils, *Chemistry & Industry*, **47**, 1334 (1928).

[3] STEINLE, Carnauba Wax, *Ind. Eng. Chem.*, **28**, 1004 (1936).

Ozokerite is a mineral wax native to the state of Utah and is plastic when heated. *Paraffin wax* occurs in certain lubricating oil fractions as the result of destructive distillation and is separated by chilling and filter pressing (see Chap. XXXVII on Petroleum). *Montan wax* occurs in peat and brown coal. When chlorinated it serves as a substitute for beeswax. The chemical production of *synthetic waxes* has been the subject of numerous patents, especially in Germany, but this field is not likely to become important in the near future.

HYDROGENATION

Hydrogenation,[2] or hardening as applied to fats and oils, might be defined as the conversion of various unsaturated radicals of fatty glycerides into more highly or completely saturated glycerides by the addition of hydrogen in the presence of a catalyst. This constitutes one of the chief commercial examples of the unit process of hydrogenation.[3] Various fats and oils, such as soybean, cottonseed, fish, whale, and peanut, are converted by partial hydrogenation into fats of a more suitable composition for shortenings, oleomargarine, and edible purposes, as well as for soapmaking and numerous other industrial uses. The object of the hydrogenation is not only to raise the melting point but greatly to improve the keeping qualities, taste, and odor of many oils.

The application of the unit process of hydrogenation to oils has been more important and far-reaching than any other improvement in this industry.

Reaction and Energy Changes.—As the reaction itself is exothermic, the chief energy requirements are in the production of hydrogen, preparation of the catalyst, warming of the oil, pumping, and filtering. The reaction may be generalized:

$$\underset{\text{Linolein}}{(C_{17}H_{31}COO)_3C_3H_5} + 3H_2 \xrightarrow{\text{Ni}} \underset{\text{Olein}}{(C_{17}H_{33}COO)_3C_3H_5}$$

Manufacture of Hydrogenated Oils.—The hydrogenation plant consists of hydrogen-generating equipment, catalyst equipment, equipment for refining the oil prior to hydrogenation, a converter for the actual *hydrogenation, and equipment for posthydrogenation treatment of the fat. These are all included in the lower part of the flow sheet of Fig. 2* The converter is pictured in Fig. 6.

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[1] LANGTON, *op. cit.*

[2] WURSTER, Hydrogenation of Fats, *Ind. Eng. Chem.*, **32,** 1193 (1940); ARMSTRONG, Fat Hydrogenation, *Chemistry & Industry*, **51,** 92 (1932).

[3] GROGGINS, "Unit Processes in Organic Synthesis," 2d ed., pp. 419*ff.*, but pp 464–469, particularly, McGraw-Hill Book Company, Inc., New York, 1938.

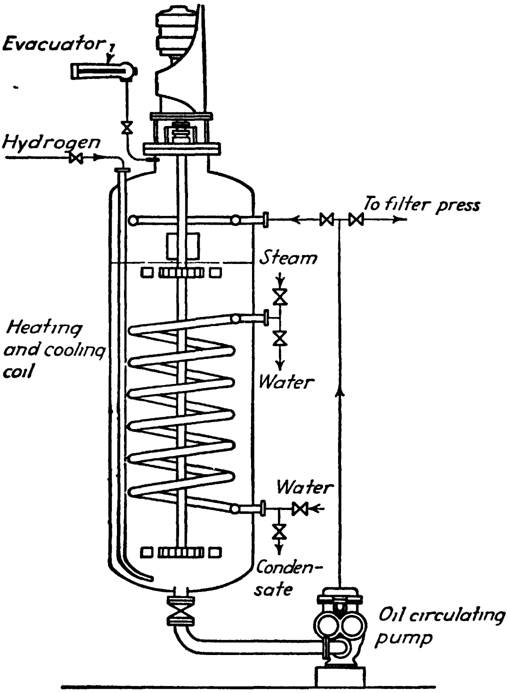

Fig 6 —Hydrogenator with internal heating and cooling coil, oil and catalyst circulating pump, and turbine-type mechanical agitator. (*Courtesy of O H Wurster*)

TABLE 4 —PURITY OF HYDROGEN

	Steam-iron process, per cent	Electrolytic process, per cent
Hydrogen	99 1	99 75
Nitrogen	0 6	0 20
Oxygen		0 05
Carbon dioxide	0 2	
Carbon monoxide	0 1	

The *hydrogen* needed is obtained by the steam-iron process, by the electrolytic decomposition of water or of salt solution (*cf* electrolytic chlorine-caustic industry), or even from cylinders of "bottle gas" where the quantity required is reasonably small. Table 4 indicates the comparative purity of hydrogen from these sources. As the presence of traces of SO_2, H_2S, or CS_2 poisons the catalyst, it is essential that the hydrogen be completely free of these substances. Also the hydrogen should carry no trace of tar or other taste-producing substances. The amount of hydrogen necessary is a function of the reduction of unsaturation, as measured by the decrease in the iodine number during hydrogenation. The theoretical quantity is about 30 cu. ft. (at 68°F.) of hydrogen per ton of oil; the actual consumption varies from 105 to 120 per cent of this figure.

The *catalyst* used commercially is almost exclusively nickel. It may be made by the modern wet reduction process, or by the older dry process. The former is employed more commonly. In the *wet process*,[1] finely divided nickel formate is suspended in a small quantity of the oil to be hydrogenated, the ratio usually being 4 parts of oil to 1 part of formate. Reduction is carried out at atmospheric pressure in a vessel equipped with a stirrer and electrical heating units. The heat is turned on and the temperature allowed to rise to 365°F. From about 302°F. on, the initial reduction begins and a small quantity of hydrogen gas is turned in to facilitate the removal of the gaseous reduction products. The reduction of the nickel, however, does not depend on the reducing action of the hydrogen. The water of crystallization is evolved as steam over a period of a half hour at 374°F., after which the temperature rises quite rapidly to 464°F., the breaking-down temperature of the nickel formate where it is held for ½ to 1 hr. The reduction is

$$Ni(HOOC)_2{\cdot}2H_2O \rightarrow Ni + 2CO_2 + H_2 + 2H_2O$$

A total time of 3 to 4 hr. is required for the process up to this point. Upon completion of reduction the charge may be pumped directly to the converter, or the catalyst cast into blocks. For this latter operation the charge is cooled to 212°F. and run into pans to solidify. This solidification is due to the hardening of the oil present by the hydrogen. The particles of nickel are thus suspended in hard fat. An alternative procedure is to run the hot catalyst-oil mixture to chilling rolls, where flakes of fat, containing catalyst, are produced. The final catalyst mixture usually contains about 7 per cent nickel by weight.

The *dry process* for producing the catalyst consists of reducing nickel carbonate or nickel hydroxide to metallic nickel in a continuous reducing furnace[2] (see Fig. 7). The nickel carbonate is prepared by precipitation with soda ash from a nickel sulfate solution. As the cost of nickel as nickel sulfate is high compared to that of metallic nickel, an electrolytic process for the preparation of nickel hydroxide from metallic nickel has been developed. The anodes are electrolytically deposited nickel, the cathode is a heavily nickeled wire cloth, and the electrolyte is a weak solution of sodium acetate. Filter-Cel is added to the electrolyte and kept in suspension by a small agitator. The passage of the current through the cell results in the formation of a precipitate of nickel hydroxide on the Filter-Cel. Either the nickel carbonate or hydroxide is reduced in the furnace of Fig. 7 by means of hydrogen. The furnace is heated with gas. The green catalyst is fed through the furnace by a helical conveyer ribbon and discharged into oil without coming in contact with air.

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[1] WURSTER, *op. cit.* This should be called the *liquid* process.

[2] SIECK, Continuous Catalyzer Reducing Furnace, *Oil & Soap*, **16**, No. 2, 24 (1939).

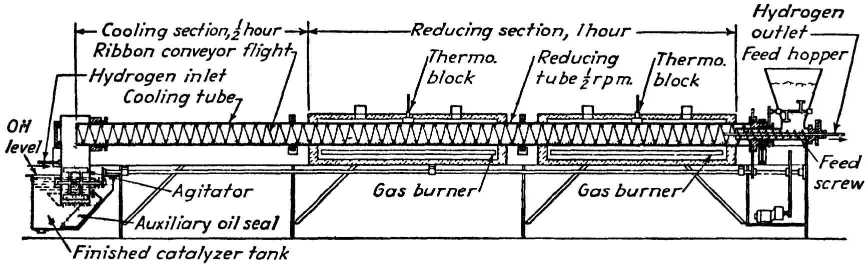

FIG. 7.—Continuous reducing furnace for producing a nickel catalyst for hydrogenation. (*Courtesy of Sieck & Drucker, Inc.*)

Hydrogenation of the Oil.—The *oil* to be hydrogenated should be free of sulfur, soaps, phosphatides, oxidized fats, water, and free fatty acids; *i.e.*, it should be fully refined. The catalyst mixture is pumped to the converter, or charged as solid from storage, in such a quantity that the final ratio will be ½ to 1 lb. of nickel per 100 lb. of oil.

The converters used are of varied design, one of which is shown here (in Fig. 6). Their main function is to mix intimately the liquid oil, the hydrogen gas, and the solid catalyst and to control the temperature of the reaction. The gas is introduced at the bottom through a distributor pipe. The oil is sprayed in at the top, withdrawn at the bottom, and repumped to the top. Heating or cooling is by either internal or external coils. A gas-circulating pump is also used quite often, as shown in Fig. 2.

The oil is charged to the converter, the heat turned on, and the circulation begun. A vacuum is applied (25 in.) to remove all air and water from the oil before the hydrogen gas is introduced. When the temperature reaches about 200 to 250°F., the vacuum is broken and the introduction of hydrogen is begun. The gas enters at a line pressure of 30 to 60 lb. per sq. in. Since hydrogenation is an exothermic reaction, the steam is now turned off, the temperature having reached about 275°F., and the subsequent rise in temperature regulated by turning cold water into the coils. Although subjected to limited variation, the best operating conditions might be said to be temperature 350 to 375°F., pressure

20 to 40 lb. per sq. in. For fish oils the temperature range is 425 to 450°F., and the converter pressure 60 to 75 lb. per sq. in.

A proper control of operating conditions is of extreme importance, especially in the case of shortenings, where it is desired to convert the less saturated constituents to olein but not completely saturate the chain. Partly hydrogenated fats having a melting point range of 95 to 97°F., an iodine number of 65, and a lardlike consistency and plasticity are manufactured on a large scale for the shortening trade.

It is necessary, especially in the case of partial hydrogenation, to have quick control tests such as by refractive index readings, to determine the course of the reaction at all times, and to know the point at which the desired hardening has been attained. When this point is reached, the hydrogen is shut off and the oil cooled to between 120 and 160°F., where it can be filtered without darkening. The clear oil is run to storage. The press cake is the catalyst, which is used over and over, either alone or with the addition of small quantities of fresh catalyst from time to time, until no longer active.

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CHAPTER XXIX

SOAP AND OTHER SURFACE-ACTIVE AGENTS

Soap comprises the sodium or potassium salts of various fatty acids, but chiefly of oleic, stearic, and palmitic acids. For generations its use has increased until its manufacture has become an industry essential to the comfort and happiness of civilized man. We may well gage the advance of modern civilization by the per capita consumption of soap.

The oils and fats needed for the saponification are no longer the waste fats from the cooking of the primitive household. The South Seas send their coconut oil, the polar seas contribute their whale oil, the cotton plantations of the Southland yield a fine cottonseed oil, the Mediterranean lands produce their olive oil, the meat-furnishing establishments collect every scrap of fatty tissue for the fat-rendering factory. Indeed, oils and fats from all over the world enter into the mammoth kettles of this soap-conscious modern civilization. Even recovered fats from garbage-disposal plants are used to satisfy the demand for soap fat. But this may not be the end of the story. Already work is under way, aiming to convert petroleum hydrocarbons into raw materials for soap. It may not be such a long distance from kerosene to detergents, with the magical help of modern research.

Historical.—Soap itself was never actually "discovered," but instead gradually evolved from crude mixtures of alkaline and fatty materials. It was mentioned as early as the first century by the elder Pliny, who described both hard and soft soap. A fully equipped soap factory was found in the ruins of Pompeii. Soap was first produced in sufficient quantities to call it an industry in the thirteenth century, using olive oil as the starting material. By the time of Queen Elizabeth, England could boast of many soap houses.

About the start of the nineteenth century the French chemist, Chevreul, showed that soap formation was really a chemical reaction and not a mere mechanical mixing of fat and alkali. Domeier completed his researches on the recovery of glycerine from saponification mixtures in this period. The alkali required was obtained by the crude leaching of wood ashes or from the evaporation of the naturally occurring alkaline waters, such as from the Nile River. LeBlanc's discovery of a method for producing lower priced sodium carbonate from sodium chloride was probably the most important in the entire history of soap manufacture.

The basic process for soapmaking has been practically the same for 2,000 years! Oils and fats are saponified with an alkali, and the soap is subsequently salted out from the spent lye. The major changes in the industry have been in the pretreatment of the fats and oils, in actual plant procedure, and in the processing of the finished soap. Thus the modern hydrogenation of oils frequently has furnished the soapmaker with new raw materials and substitutes for the older, more expensive fats and oils.

Plant procedure itself has exhibited the greatest changes in the last few years. More and more powdered soap is being produced every year, not by the older grinding process, however, but by spraying. The mills formerly used for toilet soaps are being replaced by plodders, the latter performing all the functions of the former. To keep the soap whiter, kettles are being made with the upper sections, at least, of stainless steel or Monel and are kept covered while in operation. Inhibitors such as sodium silicate[1] are added to batches to prevent decomposition and subsequent discoloration of the product. A more drastic improvement has been the rapid saponification process, which permits the production of soap from the original raw materials in only a few hours.

In America the production of soap has been almost entirely a batch process. However, processes for the continuous *saponification* of fats and oils have reached the small-plant stage, and the continuous *splitting* or *hydrolysis* of fats is already in operation in several plants. Indeed, for over 10 years a well-known European soap (Persil) has been made by neutralizing fatty acids with soda ash. The future may well see the wider commercial adoption of continuous soap production, starting with fatty acids and not fats as the initial raw material.

Uses and Economics.—It is a matter of common information that the chief use of soap is as a cleansing agent in the home and laundry. However, if soaps are defined broadly as either alkali or heavy metal salts of nonvolatile fatty acids, we find that there are numerous industrial applications for these salts as well, such as in textile mills, in the cosmetic industry, in the pharmaceutical field, and in the manufacture of tooth pastes, lubricants, emulsions, etc

The soap industry is a large one, embracing 595 plants in the United States, with products valued by the U.S. Bureau of the Census at $302,634,474 in 1939, and giving employment to 17,349 men and women. Table 1 gives a breakdown of the principal sales items.

The properties of the various soaps are much dependent upon their solubility in water and the lowering of surface tension with consequent improved wetting-out characteristics of the soluble members. From Table 2 it can be seen that some soaps, such as the potassium and sodium salts, are quite soluble, while the calcium and aluminum soaps are insoluble in water and, indeed, are water repellents, being consequently employed (in nonaqueous solutions) for waterproofing textiles and walls.

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[1] Sodium silicate also lessens corrosion, as in metal containers, and simultaneously exerts its own detergent action. *Cf.* Bolton, Value of Silicate of Soda as a Detergent, *Ind. Eng. Chem.*, **34**, 737 (1942).

TABLE 1.—MAIN PRODUCTS OF THE SOAP INDUSTRY FOR 1939[a]

	Pounds	Cents per pound
Bar soap:		
Toilet soap	409,115,770	16.1
Laundry soap, white	660,663,421	4.5
Laundry soap, yellow	577,900,473	4.7
Packaged and bulk:		
Granulated, powdered, and sprayed soaps	892,654,659	8.4
Soap chips and flakes	418,478,940	8.2
Washing powders	242,121,887	3.5
Cleaning and scouring powders with soap	186,149,836	4.1
Miscellaneous:		
Shaving soaps	5,604,814	42.7
Shaving cream	7,941,077	77.8
Liquid soap	42,781,555	8.4
Soap stock or base	4,350,109	6.5
Bar cleansers	4,953,566	6.1
Hand pastes, etc	17,913,845	5.2
Textile soaps, etc	62,988,591	7.9
Potash soaps other than textile or liquid	30,986,984	6.4

[a] U.S. Bureau of the Census, 1940.

TABLE 2.—SOLUBILITIES OF VARIOUS PURE SOAPS
(At 25°C. Grams per 100 g. of water)

	Stearate	Oleate	Palmitate	Laurate
Sodium	0.1[a]	18.1	0.8[a]	2.75
Potassium	.....	25.0	.....	70.0[a]
Calcium	0.004[b]	0.04	0.003	0.004[b]
Magnesium	0.004	0.024	0.008	0.007
Aluminum	*i*	*i*	*d*	

[a] Approximate.
[b] Solubility given at 15°C. only.
i indicates that the compound is insoluble.
d indicates decomposition.

The uses of some of the nonalkali metal soaps are important. Ethanolamine and triethanolamine soaps are employed in dry cleaning and cosmetics. The former industry also uses appreciable amounts of ammonia soaps. Zinc and magnesium stearates are in face powders, while aluminum soaps are employed in printing inks, waterproofing textiles, and polishing materials. Rosin soap is a widely used sizing for paper. Large amounts of soap are employed as an emulsifying agent in the polymerization step in the manufacture of synthetic rubber.

MANUFACTURE

The basic chemical reaction in the making of soap may be expressed as *saponification:*

$$\underset{\substack{\text{Caustic}\\\text{soda}\\\text{solution}}}{3NaOH} + \underset{\substack{\text{Glyceryl stearate,}\\\text{important fat}\\\text{constituent}}}{(C_{17}H_{35}COO)_3C_3H_5} \rightarrow \underset{\substack{\text{Sodium stearate}\\\text{solution, important}\\\text{soap constituent}}}{3C_{17}H_{35}COONa} + \underset{\text{Glycerine}}{C_3H_5(OH)_3}$$

In recent years the tendency has been to split or *hydrolyze* the fat and then, after separation from the valuable glycerine, *neutralize* the fatty acid with soda ash solution.

$$\underset{\text{Glyceryl stearate}}{(C_{17}H_{35}COO)_3C_3H_5} + 3H_2O \rightarrow \underset{\text{Stearic acid}}{3C_{17}H_{35}COOH} + \underset{\text{Glycerine}}{C_3H_5(OH)_3}$$

$$\underset{\text{Stearic acid}}{2C_{17}H_{35}COOH} + \underset{\text{Soda ash}}{Na_2CO_3} \rightarrow \underset{\text{Sodium stearate}}{2C_{17}H_{35}COONa} + CO_2 + H_2O$$

Although stearic acid is written in these reactions, oleic, lauric, palmitic, or other constituent acids of the fats used could be substituted. Reference to Table 1, Chap. XXVIII, will give the fatty acid composition

TABLE 3.—PRINCIPAL MATERIALS CONSUMED BY THE SOAP AND GLYCERINE INDUSTRIES IN 1939[a]

Chemicals:	
Alcohol (denatured) (1937)	210,000 wine gal.
Soda ash (58 per cent)	260,000 tons
Sodium silicates (40°Bé.) (1937)	160,000 tons
Caustic soda (76 per cent)	125,000 tons
Salt (1937)	46,000 tons
Sodium phosphates (1937)	39,500 tons
Sulfuric acid (50°Bé.) (1937)	8,000 tons
Lime (1937)	7,000 tons
Hydrochloric acid (100 per cent) (1937)	4,000 tons
Sodium sulfates (1937)	3,000 tons
Ammonia (1937)	300 tons
Fats and oils:	
Inedible tallow	786,500,000 lb.
Whale and fish oils	107,900,000 lb.
Coconut oil	396,900,000 lb.
Cottonseed foots, etc	3,000,000 lb.
Palm oil	84,900,000 lb.
Palm kernel oil	200,000 lb.
Greases	256,900,000 lb.
Olive foots and inedible oil	16,500,000 lb.
Babassu oil	41,200,000 lb.
Others	131,000,000 lb.

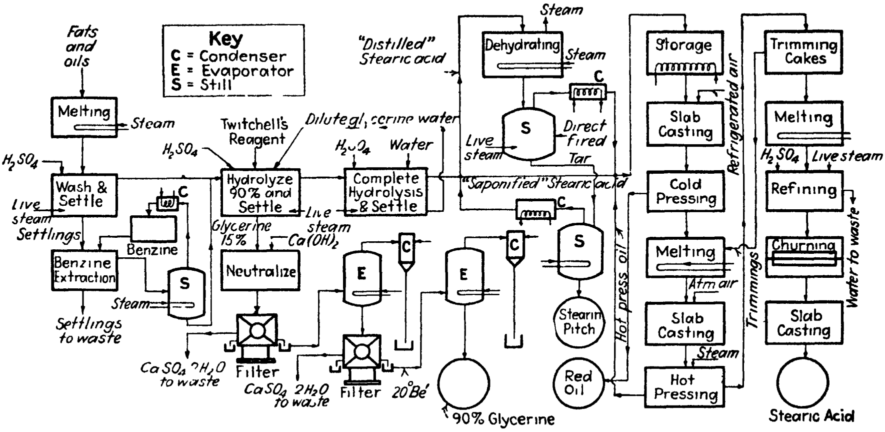
[a] U.S. Bureau of the Census.

of various fats and oils. It should be pointed out that the fats and oils of commerce are not composed of the glyceride of any one fatty acid but of a mixture. Furthermore, as the solubility and the hardness of the sodium salts of the various fatty acids differ considerably, so the soapmaker chooses his raw material according to the properties desired, with due consideration to the market price.

Raw Materials.—*Tallow* is the principal fatty material in soapmaking, the quantities used representing 40 per cent of the total oils and fats consumed by the industry, as shown by Table 3. It contains the mixed glycerides obtained from the solid fat of cattle by steam rendering. This solid fat is digested with steam, the tallow forming a layer above the water where it can be easily removed. Tallow is usually mixed with coconut oil in the soap kettle, in order to reduce the hardness and to increase the solubility of the soap. *Coconut oil* is the second most important source of soapmaking material, representing about 25 per cent of the total fats and oils consumed by the industry. As the soap from coconut oil is firm and lathers well, this oil is almost always an important constituent of household soaps. It contains large proportions of the very desirable glycerides of lauric and myristic acids, as well as smaller amounts of oleic, stearic, palmitic, and similar acids. The crude oil is treated with NaOH solution, settled, separated, and bleached. The soaps prepared from this oil have excellent lathering qualities and are often processed by the cold-made procedure. *Palm-kernel oil* and *Babassu-nut oil* are very similar in character to coconut oil. Saponification of either produces soaps very similar to those of coconut oil. *Palm oil* resembles tallow. *Fish oils* amounted to over 8 per cent of the oils used in soapmaking in 1939. These oils are frequently hydrogenated before use to improve odor, to harden, and to stabilize against rancidity. *Greases* are obtained from hogs and the smaller domestic animals, many of them diseased, or from garbage, and are an important source of glycerides of fatty acids. They are refined by steam rendering or by solvent extraction. They are seldom used without blending with other fats and, in some cases, are treated so as to free their fatty acids which are used in the soap kettle instead of the grease itself. Denatured *olive oil* is used for soap, but most of it is sold undenatured for edible purposes. *Cottonseed oil* is employed less in soaps than formerly. *Soybean oil* makes an off-colored soft soap.

Free fatty acids, including red oil, stearic acid, and the fatty acids from coconut oil, corn oil, cottonseed oil, and certain greases, are employed for soapmaking by neutralization with soda ash solution. The stearic acid obtained is also the raw material for candles. The Twitchell process, generally used to furnish these fatty acids, is an acid hydrolysis of the fats in the presence of naphthalene-sulfonic acid (Twitchell's reagent).[1] This is illustrated in Fig. 1, which also shows the steps leading to the separation of the mixed free fatty acids into a double-pressed stearic acid, red oil (mainly oleic acid), and stearin pitch. The latter is employed for roofing and other coatings. The glycerine resulting is free from salt and is higher in concentration (15 per cent) than in spent soap lye (5 to 8 per cent).

In outline, the purified fats and oils are hydrolyzed by boiling 12 to 48 hr. in lead-lined tanks with about 1 or 1½ per cent of Twitchell's reagent, on weight of fat, and some 66°Bé. sulfuric acid diluted 1:1 with water. As shown in the flow sheet (Fig. 1), this hydrolysis is carried out countercurrently in two stages. After settling and skimming off the fat, the aqueous liquor is neutralized with slaked lime, the calcium sulfate filtered off, and the glycerine liquor evaporated. It should be noted from the flow sheet that more calcium sulfate crystallizes out as the evaporation proceeds and must be filtered off. The 90 per cent glycerine is refined, as outlined in flow sheet on Fig. 5. The fatty acids are washed free of sulfuric acid and sent to the soap plant, or distilled under low vacuum, or purified by pressing, as shown in the flow sheet, to furnish the various fatty acids of commerce. A modification of the Twitchell



Fats and oils	6600 lb	Steam	18,000 lb	To Produce 1 ton double-pressed, distilled stearic acid, plus 2 tons red oil and 600 lb crude glycerine
Sulfuric acid (60° Bé)	600 lb	Refrigeration	3 tons	
Twitchell's reagent	120 lb	Electricity	10 Kw-hr	
Hydrated lime	20 lb	Direct labor	50 man-hr.	
Benzine (loss)	2 lb			

FIG. 1.—Flow sheet for stearic acid and red oil.

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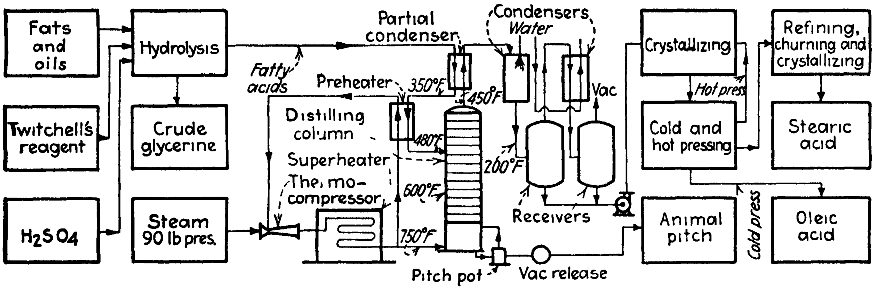
[1] Other catalysts are also used such as sulfuric acid (causes darkening), sulfonated petroleum waste acid, lime, magnesia, zinc oxide, or plain water under comparatively high pressure. See THOMSSEN and KEMP, "Modern Soapmaking," MacNair-Dorland Co., New York, 1937. For pictured flow sheet for stearic acid and red oil, see *Chem. & Met. Eng.*, **50,** No. 9, 132 (1943).

process is the Goranflo[1] process, which is a method for fatty acid distillation under vacuum, employing superheated steam (see flow sheet of Fig. 2). In addition to the Twitchell process, hydrolysis may be carried out in an autoclave (see Glycerine, page 614) in the presence of lime and water, or by high-pressure, high-temperature countercurrent liquid-liquid extraction.[2]

The soapmaker consumes large quantities of caustic soda, salt, soda ash, and caustic potash, as well as sodium silicate, sodium bicarbonate, and trisodium phosphate as shown in Table 3. The inorganic chemicals added to the soap, the so-called *alkalinity builders*, decrease the cost of the soap product without decreasing its efficiency. Appreciable quantities of rosin are employed to increase the cleaning and lathering properties of laundry soap.



Note: For details of hydrolysis, separation of acids and final purification see flowsheet, Chem and Met, p 340, June, 1934 (Vol 34)
Steam (750 deg F), 0 695 lb per lb stock charged, recovery efficiency, 90 percent plus Chart based on fatty acids of about 25 percent palmitic, 25 percent stearic, 50 percent oleic

FIG. 2.—Fatty acid production—Goranflo process.

Energy Changes, Unit Operations, Unit Processes.—The energy requirements that enter into the cost of producing soap are relatively unimportant in comparison to the cost of raw materials, packaging, and distribution. The energy required to move some of the fats and oils to the soap factory is occasionally considerable, though in these competitive days soap plants are being placed where oils and fats are primarily available. The reaction that goes on in the saponification kettle is exothermic, but much steam is employed to raise and maintain the entire mass at boiling temperature and to ensure an efficiently rapid reaction. However in large-scale saponifications employing appreciable quantities of coconut oil, comparatively small amounts of steam are required.

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[1] GORANFLO, Distillation and Purification of Fatty Acids, U.S. Pat., 1951241 (1934).

[2] ITTNER, Chap. 42, p. 1541 of "Rogers' Manual of Industrial Chemistry," 6th ed., D. Van Nostrand Company, Inc., New York, 1942. Also ITTNER, U.S. Pats., 2139589; 2221799; EISENLOHR, U.S. Pat., 2154835 (1939).

The following are the principal *unit operations* (Op.) and *unit processes* (Pr.) into which the making of soap can be divided:

Transportation of fats and oils (Op.).

Transportation or manufacture of caustic soda (Op. or Pr.).

Melting of fats and pumping to soap kettle and charging of 12 per cent NaOH (Op.).

Saponification of fatty acid glyceride, forming soap and glycerine, usually conducted hot and under agitation (Pr. and Op.).

Soap salted out and grained (Pr.).

Lyes separated and soap washed (Op.).

Rosin, sodium silicate, etc., mixed with soap (Op.).

Soap cooled and solidified in frames (Op.).

Soap put through finishing procedures (Op.): drying, cake forming, wrapping, and packaging.

Methods of Manufacture.—The manufacture of soap will be discussed under the following general headings: full-boiled process, half-boiled process, cold-made process, carbonate saponification, and other processes.

Full-boiled Process.—The full-boiled procedure is the one most generally employed in soapmaking. It is represented by the flow sheet of Fig. 3, and consists of a series of so-called *changes,* or steps, including several brine changes, a "strengthening" change (also known as a *strong* change), and a finishing change. These changes may be broken down into unit operations or unit processes as outlined above. Most toilet soaps and laundry soaps are made by this process, which is distinguished from the half-boiled process by the fact that it is carried out in *several* boiling stages, or changes, and with eventually an excess of alkali which enters the following batch. In this procedure the required mixture of fats and oils is melted, settled, filtered, and pumped to the kettle, as detailed in the flow sheet on Fig. 3.

If toilet soap is being made, the mixture is about 75 per cent tallow and 25 per cent coconut oil; in a white laundry soap the proportions would be approximately 30 per cent coconut oil and the remainder tallow and greases (light-colored). *Yellow* laundry soaps have a small percentage of rosin incorporated, to increase the lathering and cleansing ability.

The soap kettles are 15 to 30 ft. in diameter and may be twice as deep. Formerly they were built of low-carbon steel but now, to lessen discoloration of soap, they very often have at least their top sections lined with Monel, nickel-clad steel,[1] or stainless steel. They are equipped with both open and closed steam coils, a bottom liquor outlet, and a swing pipe for pumping out the soap. The open steam coil is for agitation and the closed one for the boildown on the strong change.

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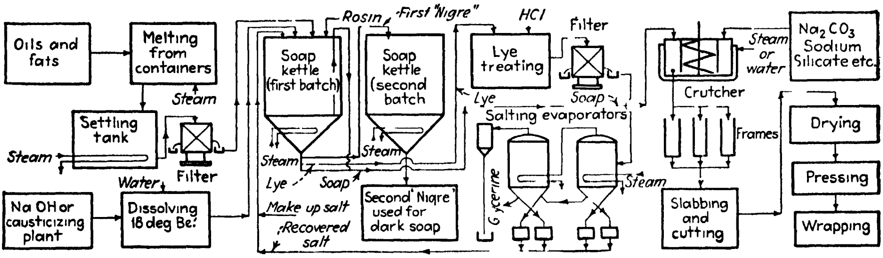
[1] Cox, Corrosion of Metals in the Soap and Allied Products Industries, *Ind. Eng. Chem.*, **30**, 1349 (1938).

After the mixture of fats is melted, the caustic soda solution (18°Bé.)[1] is added followed by agitation and heating with an open steam jet. Small portions of caustic are added from time to time, as long as the fats will react with them. After 3 or 4 hr. the paste becomes smooth and creamy and is ready for graining. This is done with recovered and make-up salt, NaCl, either granular or as a strong brine solution. The salt is added to the boiling soap until a sample on a trowel separates distinctly into soap and spent lye. About 10 to 12 per cent sodium chloride concentration is usually necessary. The steam is turned off and the kettle settled. This operation requires at least 3 hr. and frequently many more. The lyes, containing from 1 to 8 per cent glycerine and 5 to 15 per cent NaCl, settle to the bottom and are drawn off. The soap is heated and boiled once more. Water is added gradually until the kettle mass becomes smooth again, thus dissolving any glycerine and salt retained by the soap. This condition is known as *closed* soap. Further quantities of fats and caustic are sometimes added at this point. If so, they should be boiled, grained, and separated as described above. If laundry soap (yellow) is being made, rosin is added, either directly or as rosin soap. The latter is prepared by previously neutralizing the abietic acid of the rosin with soda ash (which is cheaper than caustic soda), forming a resinate. After adding any needed caustic and boiling, the kettle mixture is settled to permit removal of the aqueous solution which contains the residual glycerine. This completes the so-called *brine* changes.



Oils, fats	653	lb
Caustic soda (76 per cent Na_2O)	111	lb
Rosin	90	lb
Salt (make-up)	4	lb
Steam	2	tons
Water	230	gal
Soda ash (58% Na_2O)	37	lb
Sodium silicate (18°Bé)	822	lb

Per ton of a typical laundry soap (Plus 70 lb of 80% glycerine)

FIG. 3.—Flow sheet—laundry soap.

The last traces of fat and oil are now saponified by means of a strong, or strengthening, change. This is generally carried out on the third day.

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[1] 18°Bé. caustic soda is equivalent to 12.6 per cent NaOH. See tables in Perry, *op. cit.*, pp. 425 and 93.

The soap is brought to a boil once more, water added until the soap is closed, and then lye of about 25°Bé.[1] run in at such a rate as not to cool the mass. The soap is not soluble in the strong alkali. After it has become "grainy" once more, the steam is shut off and the kettle settled for 3 or 4 hr. The lye is run off and used in the initial saponification of a new batch of fats and oils.

The mixture is ready for the finishing change on the fourth day. The soap is heated again and water added until the mass "closes." Boiling is continued until the soap, when tested with a heated trowel, flows off in a thin, transparent sheet. This indicates that the boil is in such condition that the soaps of the higher fatty acids will separate from those of the lower fatty acids. The mass is then settled, during which time it separates into three layers. The top layer is neat soap, the intermediate layer is nigre which is a dark, strongly alkaline soap, and the lower layer is a mixture of soap and lye. The upper layer is removed by pumping out the soap through a skimmer pipe. The nigre may be degraded and incorporated in cheaper, darker grades of soap, but it generally enters into the next batch. The small bottom layer follows the nigre. The neat soap is now ready for further treatment. This finishing change frequently consumes several days' time to ensure complete separation.[2]

If white laundry soap is being made, the soap is run to a crutcher, which is a special type of steam-jacketed agitator.[3] Here soda ash, silicate of soda, and some inexpensive deodorant or perfume is added, a typical formula being soap, 700 lb.; sodium silicate, 400 lb.; perfume, 6 oz. Yellow laundry soaps contain soda ash, borax, or sodium silicate for builders, the latter being present in an amount equal to 25 to 35 per cent of the weight of the finished bar.

The mixture is now run to frames, of which a soap factory has a great number. These are boxes about 1 ft. wide, 4½ to 5 ft. long, and 3½ ft. high, with removable sides. Here the soap is allowed to cool for 3 to 5 days. The frames are then stripped, the soap is slabbed and sent to cutting tables, where taut wires cut the slab into blank cakes. These are dried at about 100°F., pressed into finished cakes with a trade-mark, and wrapped.

Toilet soaps require a slightly different procedure. The kettle soap is first dried in an automatic drier consisting of a series of two or three rolls, a drying chamber, and a cooler compartment. The rolls, which are chilled, roll the soap into large flat layers, which are cut into ribbons by a series of needlelike protrusions on one of the rolls. These ribbons are removed by a doctor knife and conveyed to the air-drying compartment in which they remain from 20 to 30 min. They are then cooled and the resulting flakes (containing from 12 to 15 per cent of water) run to the amalgamator, a mixer in which the perfume, medicinals, or other additions are incorporated. From here the mixture passes to the mill, which consists of four or five granite or iron rolls rotating at increasing speeds. The iron rolls are chilled. The soap is taken off the last roll as thin ribbons approximately ¾ in. wide and fairly short. These are dropped to the plodders, where a spiral screw forces the soap to the nozzle at the far end. The plodder is water-cooled, except for the very end of the nozzle, which is heated to give a slight polish to the soap. The soap emerges as a long, continuous bar which is cut into the desired blanks and pressed with a trade-mark into small bars. All scrap soap is reworked and reprocessed.

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[1] Equivalent to 18.6 per cent NaOH.

[2] For a study of the troublesome *middle soap* sometimes formed in the soap boiling process, *cf.* Ferguson and Richardson, *Ind. Eng. Chem.*, **24,** 1329 (1932). Neat soap, middle soap, and nigre are different phases of the three-component system of soap, water, and salt.

[3] Pictured in Perry, *op. cit.*, p. 1552

The full-boiled process is used to make soap in a great many different forms, *e.g.*, soap flakes and chips, spray-process soaps, and floating soaps. The flakes and chips are made by breaking up thin ribbons obtained from the rolls, in a drum equipped with prongs. The final product contains about 11 per cent moisture. Spray-process soaps are in the form of granules or beads. These are made by spraying hot melted soap from the crutcher into a tower where it drops countercurrent to an upward stream of warm, dry air. If a vacuum tower is used, the soap forms small beads of low density. Soda ash is often added and serves as a water softener, detergent, and drier for the soap, forming $Na_2CO_3 \cdot 10H_2O$. Floating soaps are prepared from suitable stock by mixing air into the hot soap in the crutcher by reversing the mixing screw and at a temperature around 175°F.

Half-boiled Process.—By means of this process the fats and oils are heated with just the required amount of alkali and the saponification is allowed to go to completion. All glycerine formed remains in the soap. The nigre is not separated out. The product is inferior to full-boiled soap but more economical to manufacture. Pumice soaps, some floating soaps, and certain soft potash soaps can be prepared ~~by this~~ process.

Cold-made Process.—This is undoubtedly the simplest method of making soap. It is very similar to the half-boiled process, any differences being largely a matter of temperature. The fats used must, however, be purer, the lye of *exactly* the correct proportion ~~and~~ concentration, and the ~~temperature control rigid.~~ Some potash soft soaps are prepared by this process, but it is generally used to produce ~~cold-made~~ coconut-oil and olive-oil soaps. A typical batch follows: 700 lb. of preheated coconut oil are sent to a crutcher maintained at 80 to 90°F., and 400 lb. of 36°Bé. caustic added. The resulting creamy mass is crutched anywhere from 10 to 60 min. Perfume and sodium hydrosulfite (an antioxidant) are added, and the mixture is run into frames, where saponification is completed. The frames are maintained at a temperature of around 110°F. After 24 hr. the frames are removed from the hot room and cooled for 72 to 96 hr. at room temperature. There are several major objections to this process: none of the glycerine can be recovered, all scrap soap must be discarded, and discolored soaps often occur, as the result of incomplete saponification.

Carbonate or Direct Neutralization.—This method neutralizes with alkali, usually soda ash, the free fatty acids obtained from neutral fats by the Twitchell or autoclave process. Soap made by this process is on the increase. Dr. Ittner[1] writes, "It is highly probable that this method of soap manufacture will gradually crowd out most other methods." In one method of carrying out the process, a 30°Bé. soda ash solution[2] is run into a kettle and melted fatty acids sprayed in on top of the soda ash solution, which has been previously heated by means of steam coils. The acid and alkali react immediately, carbon dioxide being liberated. The mass is boiled for a short time, and then caustic soda is added to neutralize the small portion of neutral fat which was brought in with the free acids. If the glycerine from this neutralization is wanted, the kettle is next grained with salt in the usual manner. The contents of the kettle are settled and finished.

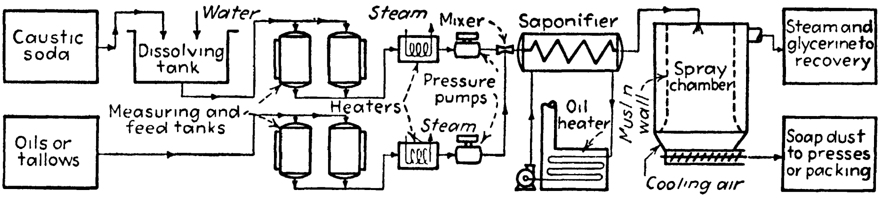

FIG. 4.—Continuous saponification.

Other Processes.—At present, there are several commercial units employing a continuous saponification process. A typical process is depicted on the flow sheet on Fig. 4, and the manufacture of soap in a continuous process is a probable large development of the very near future. In the process shown, the fats and oils are saponified with 50 per cent caustic at 480 to 570°F., under a pressure of 800 to 1,500 lb. per sq. in. The reaction chamber is a short 8-in. tube. The saponified mixture is passed into muslin-lined spraying chambers from which the steam escapes while the soap is retained. All but about 2 per cent of the glycerine is vaporized at the same time. The soap obtained is in the form of fine powder. By use of suitable nozzles, granulated soap can be prepared. It is also possible to use the free fatty acids instead of the neutral fats in the process.

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[1] ITTNER, "Rogers' Manual of Industrial Chemistry," *op. cit.*, p. 1553.

[2] This is equivalent to 26 per cent Na_2CO_3. *Cf.* PERRY, *op. cit.*, pp. 93 and 425.

Rapid saponification has received much attention in recent years. The reaction is carried out in a crutcher, no kettle being required. Fatty acids, or neutral fats, may be used as starting materials and as high as 50°Bé. caustic for saponification. Reaction is complete in as little as 2 hr. Since the greater part of the glycerine is left in the product, many of the soaps produced are superior to full-boiled soaps. However, the value of the glycerine itself may far outweigh its ability to increase the quality of the soap, in which case the entire process is uneconomical.

Typical Soaps.—Table 1 presents the classification adopted by the U.S. Bureau of the Census for the soap industry. However, frequently these more detailed divisions are separated into three main classes: toilet soaps, household soaps and industrial soaps. The household soaps comprise the various laundry soaps and many varieties of soap chips and powders. These different soaps can frequently be made by one or more of the previously described procedures.

Except for the purest of toilet soaps, various chemicals are added as "builders" economically to improve their over-all cleansing quality. Practically all soap as merchandised contains from 10 to around 30 per cent of water. If soap were anhydrous, it would be too hard to dissolve easily. Almost all toilet and household soaps contain perfume, even though it is not apparent, serving merely to disguise the original soapy odor. Toilet soaps are made from selected materials and usually contain only 10 to 15 per cent moisture with very little added material except for the perfume and perhaps a fraction of a per cent of titanium dioxide as a whitening agent.

A typical composition of a laundry soap can be inferred from the materials given on the bottom of Fig. 3. These soaps contain up to 30 per cent moisture. Household chipped or flaked soaps are generally a little lower in moisture content than the corresponding bar soaps; a representative composition would be as follows: moisture, 10 to 20 per cent; soap, 50 to 60 per cent; tetrasodium pyrophosphate, 15 per cent; sodium metasilicate, 7 per cent; soda ash, 8 per cent.

Shaving soaps contain a considerable proportion of potassium soap with an excess of stearic acid, the combination giving a slower drying lather. The "brushless" shaving creams contain stearic acid and fats with much less soap. The soft or liquid soaps at one time were almost all potash soaps. Now they are mostly soda soaps with the proper choice of the fatty acid to give the desired fluidity.

SURFACE-ACTIVE AGENTS

(Other than Soaps)

The modern concept of surface-active agents[1] includes soaps, detergents, emulsifiers, wetting agents, and penetrants. These all owe their activity to a modification of the properties of the surface layer between two phases in contact with another. Most of the surface-active agents are a combination of water-attracting or hydrophilic groups on the one hand, with water-repelling or hydrophobic groups on the other.

Around 1930 a number of synthetic detergents began to appear on the market. These were principally sodium salts of fatty alcohol sulfates and hence not soaps. Their advantage lay in the fact that they did not form precipitates with the calcium and magnesium hardness in waters and so did not require soft water for their use. In the past few years many new compounds have been added, until an up-to-date list of modern wetting agents and detergents presents quite a formidable appearance.[2] These compounds are frequently combinations of aromatic rings or of fairly long chain aliphatic groups that are hydrophobic, and either sulfate or sulfonate groups that are hydrophilic. They increase wettability of materials as follows: The hydrophobic group attaches itself to the grease or oil to be solubilized, leaving the hydrophilic group free to attract water.[3] Since the properties of a good wetting agent are closely interwoven with those of a good detergent, little or no attempt will be made to distinguish between them. However, in the case of some of the compounds discussed below, their utility as one far outweighs their usefulness as the other.

Sulfated or *sulfonated oils* are sulfated aliphatic esters which may be obtained by treating castor, corn, olive, lard, or rape oil with 27.5 per cent sulfuric acid, employing so-called high sulfonation,[4] quick sulfonation, or low-temperature sulfonation. These products have long been known as *sulfonated oils*, but the bond is mostly through the oxygen of a sulfate group. The principal commercial product is the sulfonated castor oil, sold as *Turkey-red oil.* This should be called *sulfated* castor oil as the principal constituent has the following formula, for one third of its molecule:

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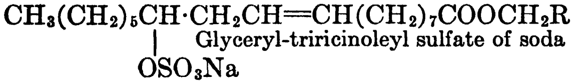
[1] These might all, with soap, be called *surface-active agents*. For an excellent description, classification, and listing of such agents, see Snell, Surface Active Agents, *Ind. Eng. Chem.*, **35**, 107 (1943); Van Antwerpen, Surface Active Agents, *Ind. Eng. Chem.*, **35**, 126 (1943). For a modern presentation of detergency, see pp. 261–266 of Lewis, Squires, and Broughton, "Industrial Chemistry of Colloidal and Amorphous Materials," The Macmillan Company, New York, 1942.

[2] Eight hundred patents on sulfonation and sulfation, applying to the field of detergents, penetrants, and wetting agents, have been issued in the past 10 years. GOLDTHWAIT, *Am. Dyestuff Reptr.*, **23**, 569–580 (1937); VAN ANTWERPEN, *op. cit.*

[3] EVERS, Detergents and Wetting Agents, *Pharm. J.*, **140**, 326–327 (1938); MANN, Mechanism of Detergency, *Am. Dyestuff Reptr.*, **22**, 297–298 (1933). Under the subject of detergency, see also pp. 261, 265 of Lewis, Squires, and Broughton, *op. cit.* A very excellent summary article is in Snell, *op. cit.*

[4] SUNDERLAND, *Soap*, **11**, No. 10, 61–64; No. 11, 61–64; No. 12, 67–69 (1935).



$$\underset{\substack{|\\ OSO_3Na}}{CH_3(CH_2)_5CH}\cdot CH_2CH{=}CH(CH_2)_7COOCH_2R$$

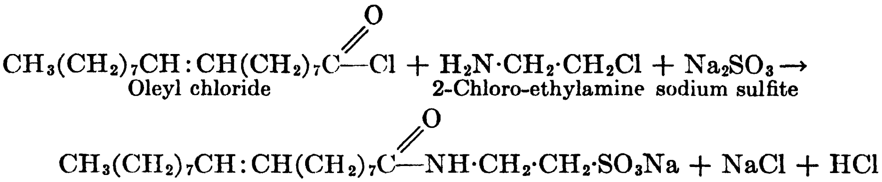
Glyceryl-triricinoleyl sulfate of soda

This product can be prepared as follows: Equal quantities of castor oil and ethylene dichloride (the latter as a diluent) are mixed and cooled. An amount of strong sulfuric acid, equal to that of the oil, is run in slowly, keeping the temperature below 60°F. Stirring is continued until a sample of the mixture dissolves clear in distilled water. A 5 per cent sodium sulfate solution is then added, equal to three times the sulfated mixture, to salt out the product. After separating into two layers, the product is washed with 25 per cent Glauber's salt solution, reseparated, neutralized with caustic, and the ethylene dichloride distilled off. The product is a light oil, marketed as 25 or 50 per cent sulfonated castor oil (percentage figures refer to water content). Such products are used in the processing and dyeing of cotton because of their dye-assisting and wetting-out qualities. However, they are poor detergents and are being replaced by sulfated fatty acids and sulfated "hymolal" alcohols.

Alkylnaphthalene-sulfonic acids and salts are being employed as surface-active agents and are known as Nekals, Alkanols, etc. These are made by alkylation of a naphthalene-sulfonic acid.

The *hymolal alcohol derivatives* are long-chain aliphatic sulfates and are sold as Gardinols or Duponols and Avirols. They are made from technical grades of lauryl, myristyl, oleyl, palmityl, and stearyl alcohols. These high-molecular weight alcohols are obtained by hydrogenation of the corresponding fatty acids prepared initially by the Twitchell process and purified by distillation. The hydrogenation is done under 3,000 lb. pressure and at temperatures ranging from 200 to 250°C., using as catalysts zinc, copper, and cadmium chromites. The alcohols are treated with sulfuric acid under moderate conditions, producing the sulfate which is then converted to the corresponding sodium salt with alkali. The commercial products consist of a mixture of these hymolal alcohols, together with an added diluent, usually sodium sulfate. Dreft is predominantly a commercial sodium lauryl sulfate (plus diluent) while Drene is the triethanolamine lauryl sulfate. The sulfated alcohols surpass soap and sulfonated oils in wetting-out, emulsifying, and detergent properties, do not hydrolyze to alkali in water, and show no tendency to turn rancid on storage. They are stable toward acids, alkalies, and salts but, most important of all, are not precipitated by the hardness (Ca and Mg ions) present to some extent in most municipal waters.

The *fatty acid amides* are other examples of efficient surface-active agents. As Snell[1] points out, these are so insoluble in water that some water-attracting group needs to be introduced. These compounds are exemplified by Igepon T which is made as follows:



$$\underset{\text{Oleyl chloride}}{CH_3(CH_2)_7CH{:}CH(CH_2)_7\overset{\overset{O}{/\!/}}{C}-Cl} + \underset{\text{2-Chloro-ethylamine}}{H_2N\cdot CH_2\cdot CH_2Cl} + \underset{\text{sodium sulfite}}{Na_2SO_3} \rightarrow$$

$$CH_3(CH_2)_7CH{:}CH(CH_2)_7\overset{\overset{O}{/\!/}}{C}-NH\cdot CH_2\cdot CH_2\cdot SO_3Na + NaCl + HCl$$

The water-attracting group in Igepon T is the sodium sulfonate mildly assisted by the substituted amide. The product is a useful surface-active agent and finds application in wetting, emulsifying, deflocculating, and foaming. The Igepon T is stable in both acid and alkaline solutions and does not give a precipitate with calcium and magnesium ions, thus lacking the two main disadvantages of soap.

GLYCERINE

Historical.—Glycerine[2] is a clear, nearly colorless liquid, having a sweet taste but no odor. K. W. Scheele first prepared glycerine in 1779 by heating a mixture of olive oil and litharge. On washing with water, a sweet solution was obtained, which on evaporation of the water gave a viscous heavy liquid, which the discoverer called "the sweet principle of fats." In 1846 Sobrero produced the explosive nitro-glycerine for the first time, and in 1868 Nobel, by absorbing it in kieselguhr, made it safe to handle as dynamite. These discoveries increased the demand for glycerine. This was in part satisfied by the development in 1870 of a method for recovering glycerine and salt from spent soap lyes.

Uses and Economics.—In 1939 the production of the various grades of glycerine was as follows: soap lye, crude, 183,610,302 lb. From this was made dynamite grade, 65,578,366 lb. and c.p. glycerine, 96,950,763 lb. The market price for glycerine (c.p.) has fluctuated over a period of years from 10 cents per pound at the depth of the depression to 60 and 70 cents per pound under 1914–1918 war conditions. The average over a long period of years is around 15 to 16 cents per pound.

Glycerine is employed for the making, preserving, softening, or moistening of a great many products. Large users of glycerine are the explosive and Cellophane manufacturers, tobacco handlers, varnish makers, and resin manufacturers. The amount consumed in Cellophane, tobacco, and resins has greatly increased in recent years. In addition, the medicinal and pharmaceutical, as well as the cosmetic trade, consumes appreciable amounts. Glycerine enters into the manufacture of antifreeze solutions, printing inks, typewriter ribbons, golf balls, photographic emulsions, and chewing gum. Its more recent applications include its reaction with phthalic anhydride (or acid) and other polybasic acids for the production of synthetic resins and plastics (glyptal resins), as a softening agent in the leather industry, and as an emulsifying and dispersing product.

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[1] SNELL, *op. cit.*

[2] The term *glycerine* is chosen because it is the technical spelling most used for the trihydroxy alcohol, *glycerol*. The spelling *glycerin* is employed by the United States

GLYCERINE MANUFACTURE

Glycerine may be produced by a number of different methods,[1] among which the following are important: (1) the saponification of glycerides (oils and fats) to produce soap; (2) the splitting of fats and oils (Twitchell, etc.) to produce soap; (3) the chlorination and hydrolysis of propylene from cracked still gases. When the price of glycerine becomes sufficiently high, fermentation glycerine may make its appearance on the market. This is borne out by the fact that during the First World War Germany produced as high as 2,000 tons per month by fermenting beet sugar in the presence of sodium sulfite. Since such glycerine is hard to purify, this procedure has been turned down by American manufacturers. Some glycerine is produced by the *autoclave process* where the fat is heated in a copper autoclave with lime, magnesia, or zinc oxide, or even by hot hydrolysis with water according to the Ittner process referred to under Fatty Acids (page 604).

Energy Changes, Unit Operations, and Unit Processes.—In recovering glycerine from the soap plants the energy requirements are mostly concerned with heat consumption involved in the unit operations of evaporation and distillation, as can be seen by the steam requirements tabulated on the flow sheet on Fig. 5. The breakdown of two procedures for glycerine is listed in the following columns:

Glycerine from spent lye:
- Chemical purification with filtration (Pr. and Op.)
- Evaporation (multiple effect) for concentration and for salt recovery (Op.)
- Steam vacuum distillation (Op.)
- Concentration (Op.)
- Decoloration (Op.)
- Redistillation (Op.)

Glycerine from petroleum:
- Purification of propylene (Op.)
- Chlorination to allyl chloride (Pr.)
- Purification and distillation (Op.)
- Chlorination with HOCl (Pr.)
- Hydrolysis to glycerine (Pr.)
- Distillation (Op.)

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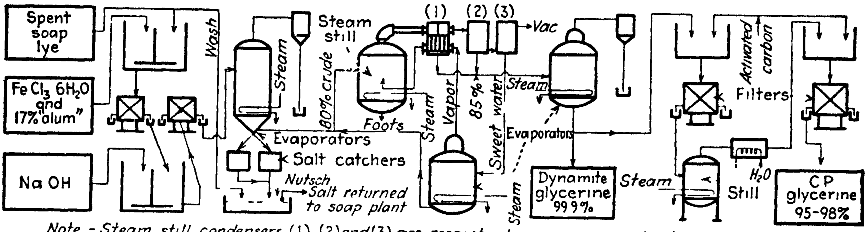
[1] Guillaudeu, Glycerine Liberation, Recovery and Refining, *Ind. Eng. Chem.*, **29**, 729–733 (1937).

Glycerine from Spent Soap Lyes.—The spent soap lyes are by-products and must be purified before recovery[1] of glycerine. A typical spent lye contains about 3 to 8 per cent glycerine, 5 to 15 per cent sodium chloride and water, together with small quantities of caustic soda, sodium carbonate, soap, fatty acids, and other organic impurities. After cooling and settling to remove much of the soap, the lye is treated to reduce the alkalinity and to remove organic impurities, in accordance with the flow sheet on Fig. 5. The lye is pumped to the first treatment tank where ferric chloride is added, in the amount determined by previous experience as being required to give maximum precipitation of hydroxyl ions and of soap. About 2.5 lb. of ferric chloride per 1,000 lb. of lye is usually required. Low-grade lyes need an additional 0.5 lb. of aluminum sulfate for 1,000 lb. of lye in order to produce a more complete removal. Since the ferric chloride used is strongly corrosive to iron and steel, it is dissolved in stoneware crocks or glass-lined tanks and added in solution to the treatment tank. Steel treatment tanks are satisfactory. A little hydrochloric acid is added to bring the lye just on the acid side to cause precipitation of metallic soap.



Note - Steam still condensers (1), (2) and (3) are respectively a vapor superheater, an air or warm water partial condenser for 85% glycerine and a cold water final condenser for sweet water

Spent lye (glycerine, 5%)	22	tons
Caustic soda	200	lb
Aluminum sulfate	22	lb.
Ferric chloride	110	lb
Activated carbon (make-up)	5 10	lb.

Steam	8,000 lb	To produce glycerine, 1 ton salt, 2 2 tons
Electricity	10 kw-hr	
Direct labor	4 man hr	
Activated carbon	5-10 lb	

FIG. 5.—Flow sheet for glycerine manufacture.

After thorough agitation in the first treatment tank the lye is filter-pressed warm and then run into the second treatment tank, where a little caustic soda is added until the lye is alkaline. This lye, filtered again, has a glycerine content of from 4 to 10 per cent, and a salt concentration of from 11 to 18 per cent. The glycerine lyes are concentrated in a single- or preferably in a double-effect evaporator. The former is used when it is desired to have a minimum amount of equipment. A double effect is preferred because the exhaust steam and water requirements are approximately half those of the single effect.

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[1] WURSTER, The Recovery of Crude Glycerine, *Oil & Soap*, **13**, 246–253, 283–286 (1936); for pictured flow sheet, see *Chem. & Met. Eng.*, **50**, No. 9, 132 (1943).

As the evaporation proceeds and as the concentration of glycerine increases, the solubility of the salt decreases and it crystallizes out. This salt, collecting in the cone of the evaporator, is periodically dropped into the empty one of the two salt catchers. The catchers, or chambers, are provided with false bottoms that catch the salt. The glycerine liquor is drained off and returned to the vacuum evaporator (by a pipe not shown in Fig. 5), after the main valve between the evaporator and the salt chamber has been closed and a vent opened to the atmosphere. The salt is removed from the catcher, centrifugated, washed, and returned to the soap plant. In some plants a large suction filter box, known as a *nutsch*, is used instead of the centrifuge. Eventually the evaporator contains the crude glycerine (80 per cent) which is either sold by small plants to refiners or refined at once.

Refining of Crude Glycerine.—The impurities present in crude glycerine include 0.1 per cent fatty acids (as soap), from 4 to 11 per cent salt, and organic impurities. These are separated by steam vacuum distillation after being made strongly alkaline with caustic soda in order to hold back fatty acids and other impurities. The 80 per cent crude is first heated to boiling with superheated steam, after which low-pressure steam is turned directly into the charge and the glycerine steam distilled under vacuum. The vapors are passed through a series of air-cooled condensers, which remove most of the glycerine and then through a water-cooled condenser, where the water and remaining glycerine are condensed (see Fig. 5). In a continuous system the procedure is similar, except that crude is fed to the evaporator and salt is continuously removed. This continuity of operation permits standardization of operating conditions and perhaps greater uniformity of product.

The 85 per cent glycerine is concentrated to dynamite grade, or it is decolorized by activated carbon, redistilled, redecolorized to the c.p. product. The sweet water (with any trimethylene glycol), containing from 1 to 2 per cent of the glycerine from the crude still, is separately evaporated, giving steam and concentrated glycerine for the crude steam still.

Synthetic Glycerine from Petroleum.—The growing market for glycerine, together with the fact that it is a by-product of soap and dependent upon the latter's production, has been the incentive for research into synthetic methods for producing this trihydroxy alcohol. Quite recently such a process was announced by the Shell Development Company.[1] The initial raw material is propylene from the debutanizers of the petroleum industry. This is chlorinated to produce allyl chloride in amounts approximately 85 per cent of theory (based on the propylene). Vinyl chloride, some disubstituted olefins, and a little dichloro-propane are also formed. (The reaction producing allyl chloride is new to organic synthesis, involving as it does the chlorination of an olefin by substitution instead of addition.) Treatment of the allyl chloride with hypochlorous acid at 25°C. produces the glycerine dichlorohydrin, $CH_2Cl{\cdot}CHOH{\cdot}CH_2Cl$, which can be hydrolyzed to glycerine. The glycerine dichlorohydrin can be hydrolyzed directly to glycerine but this takes two molecules of caustic soda, hence the more economical procedure is to react with the cheaper calcium hydroxide, taking off the epichlorohydrin as an overhead in a stripping column. The epichlorohydrin is easily hydrated to monochlorohydrin and then hydrated to glycerine[1] with caustic soda. The reactions follow:

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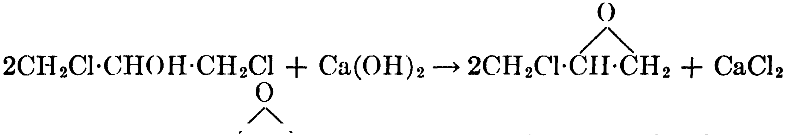
[1] WILLIAMS, Synthetic Glycerine from Petroleum, *Chem. & Met. Eng.*, **47**, 834–838 (1940); *Trans. Am. Inst. Chem. Engrs.*, **37**, 157 (1941); Economic Aspects of Synthetic Glycerine Production, *Chem. & Met. Eng.*, **48**, 87 (1941).

$$CH_3{\cdot}CH{:}CH_2 + Cl_2 \xrightarrow{510°C} CH_2Cl{\cdot}CH{:}CH_2 + HCl \text{ (85 per cent yield)}$$

$$CH_2Cl{\cdot}CH{:}CH_2 + HOCl \rightarrow CH_2Cl{\cdot}CHOH{\cdot}CH_2Cl \text{ (95 per cent yield)}$$



$$2CH_2Cl{\cdot}CHOH{\cdot}CH_2Cl + Ca(OH)_2 \rightarrow 2CH_2Cl{\cdot}CH{\cdot}CH_2\,(O) + CaCl_2$$

$$CH_2Cl{\cdot}CH{\cdot}CH_2\,(O) + H_2O \rightarrow CH_2Cl{\cdot}CHOH{\cdot}CH_2OH$$

$$CH_2Cl{\cdot}CHOH{\cdot}CH_2OH + NaOH \rightarrow CH_2OH{\cdot}CHOH{\cdot}CH_2OH + NaCl$$

The over-all yield of glycerine from allyl chloride is above 90 per cent.

Problem

A washing compound is to be made by drying a solution containing 15 per cent soap and 25 per cent sodium carbonate. During the course of the drying the sodium carbonate is converted to the decahydrate and appears in the finished product in this form. The finished washing compound contains 8 per cent free moisture. How many pounds of solution should be taken to produce 100 lb. of finished washing compound?

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[1] An excellent block flow sheet and also a diagramatic flow sheet of this procedure are available in the quoted literature. *Cf.* WILLIAMS, *op. cit.;* especially, LEVITT, Glycerine, Its Compounds and Uses, *Chem. Industries*, **50**, 34 (1942).

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CHAPTER XXX

SUGAR AND STARCH INDUSTRIES

The carbohydrates, sugar and starch, are products of our soils. They serve as man's principal energy foods and enter into countless manufacturing sequences. The present virile chemurgic movement seeks to broaden the application of these and other farm products into an ever-increasing tide of raw materials through the country's factories into manufactured consumers' goods.

SUGAR

Nature has always provided foods from her ample stores in the vegetable kingdom to supply the sweetness that man requires in his diet. The average person in the United States eats his own weight in sugar about every year and a half.[1] The world average is only one third of this. This is due not solely to his liking for the sweet taste but to the demands of an active body for fuel, since sugar supplies man with about 13 per cent of the energy required for existence. As a result, sugar refining is an enormous industry, representing in the United States alone an investment of more than $250,000,000 and paying about $100,000,000 in annual Federal taxes.

Historical.[2]—It is difficult to discover just when sugar was first known to mankind, but it seems to be generally agreed that it occurred in India many centuries before Christ. Methods for extracting and purifying the sugar from the cane were very slow in being developed, but we find record of crude methods having been brought from the East to Europe about 1400. The sugar trade between Asia and Europe was one of the most important commercial items in the early centuries. Later, cane plantations were established in northern Africa and in the West Indies.

Sugar was first extracted in North America in 1635, using cane from the West Indies, while in 1689 cane was grown on the continent. From this time on, the industry increased steadily, both in size and in quality of product. Steam-driven crushing and grinding roller mills were introduced in the latter part of the eighteenth century; the vacuum pan was invented by Howard about 1813; bone-black filtration was employed for the first time in 1815. Multieffect evaporation was proposed about

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[1] A more exact figure is 96.5 lb. per capita per year, based on 1937–1938 consumption.

[2] Horne, Sugar Industries of the United States, *Ind. Eng. Chem.*, **27**, 989 (1935).

1834, and the first suspended centrifugal was developed by Weston in 1852. A recent development has been the use of decolorizing carbons, which in several plants has been replaced by treatment with bauxite, followed by calcium hypochlorite.

Evaporation, adsorption, centrifugation, and filtration were early important and necessary steps in the manufacturing sequences for sugar, and much of our knowledge of these steps came from their application to the industry. We may say that this study of the functioning of evaporation, adsorption, centrifugation, and filtration as exemplified in sugar making helped to establish the generalized concept of unit operations.

In 1747 beet sugar was discovered, but it was not introduced into the United States until 1830, and no successful plants were operated until 1870. A great deal of time, effort, and money was expended in bringing the more complicated beet-sugar industry to the point where it could compete with cane sugar. The various tariffs imposed on raw cane-sugar imports, among other things, are responsible for the continuance of the beet-sugar industry.

The first preparation of dextrose in 1811 led to the development of the corn-sugar industry in this country. The first manufacturing began about 1872, the product being liquid glucose. It was not until 1918, however, that appreciable quantities of pure, crystalline dextrose were produced.

At the start of the present century, the Bergius process for the production of sugar by saccharification or hydrolysis of wood received its first industrial trial. A small plant for the production of alcohol was erected in South Carolina in 1910. In 1916 Bergius and Hagglund, in Germany, undertook the development of the present Bergius process, employing hydrochloric acid. In 1930 Scholler began operations with sulfuric acid, at Tornesch, Germany. As far as the United States is concerned, these processes, although chemically feasible, have proved economically unsound, owing to the abundance and low price of starch and sugar; however, they seem to be finding their place in the countries of Europe, where the scarcity of food supplies gives the products a higher value.

Uses and Economics.—In 1939 approximately 7,000,000 tons[1] of refined sugar were consumed in the United States. Of this total about 78 per cent was of cane origin and the remainder was from beet. Exports during this same period totaled 125,000 tons. Domestic consumption was distributed approximately as shown in Table 1. Included in the last item are the nonfood uses of sugar. These are very few, however, and constitute only a small amount of the total output. They include the use of sugar as a strengthening agent in lime-sand mortar, in leather tanning, in paper softening, as calcium saccharate in whipping cream and ice cream, as copper saccharate insecticide, and as sucrose octaacetate, a denaturant in ethyl alcohol.

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[1] NEMIR, "Sugar and Molasses Trade of the United States in 1939," U.S. Department of Commerce, 1940. PERRY, *op. cit.*, p. 2388, presents a map showing the location of the cane-sugar refineries in the United States. LYNSKY, "Sugar Economics, Statistics and Documents," U.S. Cane Sugar Refiners Assoc., 1938 and 1939.

Probably no other organic product of comparable purity (99.5 per cent) is offered on the retail market for so low a price as sugar. This, however, is merely a reflection of the progress and growth in refining methods due to applied chemical engineering within the industry, which has succeeded in reducing the price from the $4 a pound prevailing during the administration of John Adams to its present low level of about 5 cents per pound.

TABLE 1.—CONSUMPTION OF SUGAR IN THE UNITED STATES, 1939[a]

	Per Cent
Household and restaurant	70.0
Bread and bakers	8.2
Confectionery	6.1
Canning and preserving	5.0
Extracts and flavoring	2.6
Nonalcoholic beverages	2.4
Chocolate and cocoa	2.0
Other food products	1.5
Dairy products	1.1
Chewing gum	0.5
Tobacco	0.3
Alcoholic beverages	0.2
All other industries	0.03

[a] "Sugar and Reciprocal Trade Agreements," U.S. Tariff Commission, Washington, April, 1940.

MANUFACTURE OF SUGAR

Cane.—Sugar cane is a member of the grass family. It has a bamboo-like stalk, grows to a height of from 8 to 15 ft. and contains 11 to 15 per cent sucrose by weight. The source of the raw cane refined in the United States is portrayed in Table 2. The cane is usually planted with cuttings from the mature stalk, which sprout and produce a number of new stalks. As many as 20 successive crops or "ratoons" may be obtained from a single planting, provided conditions are favorable. The approximate period of growth of the cane is 12 to 15 months in Cuba, while nearly twice this time is required in Hawaii. Harvesting is done by hand, with large sharp knives or machetes. The workmen cut off the stalks close to the ground and then remove the top sections and leaves, which are used as cattle food or fertilizer. The remainder of the stalks is loaded on large wagons which are drawn to a railroad siding by means of oxen or tractors. The railroads take the cane to the raw-sugar plants, or *centrales* as they are called in Cuba. There can be no delay in getting the freshly cut cane to the factory, because failure to grind it in less than 2 days after cutting causes much of the sucrose to be lost by inversion into glucose and fructose.

TABLE 2.—UNITED STATES PRODUCTION AND IMPORTS OF RAW CANE SUGAR IN 1939[a]

	Thousands of short tons	Percentage
Continental United States	511	9.7
Offshore areas:		35.3
Hawaii	934	17.8
Puerto Rico	918	17.4
Virgin Islands	6	0.1
Imports to United States:		55.0
Cuba	1,872	35.5
Philippines	951	18.0
All others	79	1.5
Total	5,271	

[a] "Sugar and Reciprocal Trade Agreements," U.S. Tariff Commission, Washington, April, 1940.

The production of raw cane sugar at the factory is illustrated in Fig. 1 and may be divided into the following *unit operations* (Op.) and *unit processes*[1] (Pr.):

The cane is torn and shredded by crushers in preparation for removing the juice (Op.).

The juice is extracted by passing the crushed cane through a series of mills, each of which consists of three grooved rolls that exert a heavy pressure. Water and weak juices may be added to help macerate the cane and aid in the extraction. About 95 per cent of the juice is extracted from the cane (Op.). The spent cane (bagasse) is either burned for fuel or used to manufacture insulating material.

The juice is screened to remove floating impurities and treated with lime to coagulate part of the colloidal matter, precipitate some of the impurities, and change the pH (Op. and Pr.). Phosphoric acid may be added because juices that do not contain a small amount of phosphates do not clarify well. If acid is added, an excess of lime is used. The mixture is heated with high-pressure steam and settled in large tanks called *clarifiers* or in continuous settlers or thickeners (Op.).

To recover the sugar from the settled-out muds continuous rotary drum vacuum filters are generally used although plate-and-frame presses may be employed (Op.). The cake constitutes 1 to 4 per cent of the weight of cane charged and is used as manure.

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[1] See also the pictured flow sheet, Raw Sugar from Cane, *Chem. & Met. Eng.*, **48**, No. 7, 106 (1941); Process Flow Sheet for Raw Sugar House, "Rogers' Manual of Industrial Chemistry," 6th ed., p. 1340, D. Van Nostrand Company, Inc., New York, 1942; RIEGEL, "Industrial Chemistry," 4th ed., p. 411 for flow sheet, Reinhold Publishing Corporation, New York, 1942.

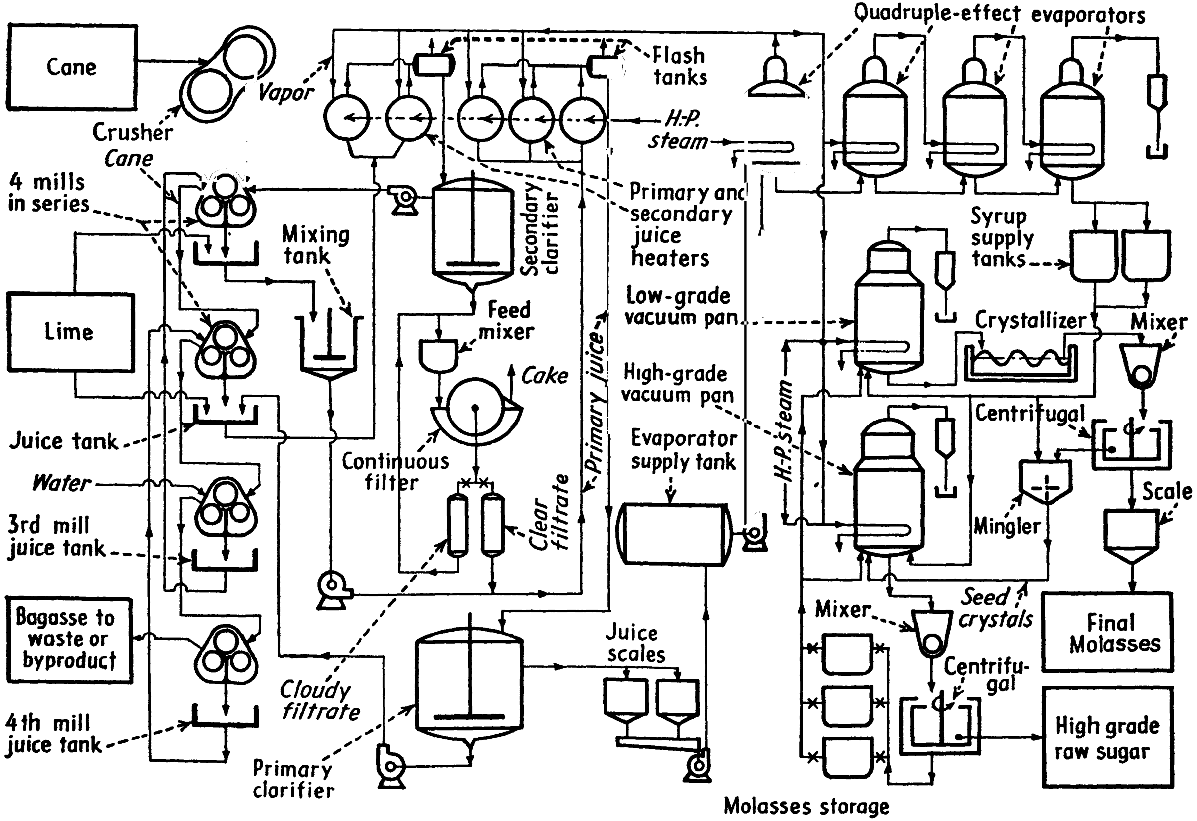

FIG. 1.—Flow sheet for raw cane sugar.

The filtrate, a clarified juice of high lime content, contains about 85 per cent water. It is evaporated to approximately 40 per cent water in triple- or quadruple-effect evaporators[1] (Op.).

The resulting dark-brown, viscous liquid is crystallized in a single-effect vacuum pan. The sirup is concentrated until crystal formation begins (Op.).

The mixture of sirup and crystals (massecuite) is dumped into a crystallizer which is a horizontal agitated tank equipped with cooling coils. Here additional sucrose deposits on the crystals already formed, and crystallization is completed (Op.).

The massecuite is then centrifuged to remove the sirup. The crystals are high-grade raw sugar, and the sirup is retreated to obtain one or two more crops of crystals. The final liquid after reworking is known as *blackstrap* molasses (Op.).

The raw sugar (light brown in color), containing approximately 97 per cent sucrose, is packed in bags and shipped to the refinery (Op.).

The molasses[2] is shipped to the United States and other countries in full tank steamers and is used as a source of carbohydrates for fermentation and for cattle feed (Op.).

Cane Sugar.—The sacks of raw sugar, weighing 300 to 330 lb., are unloaded from the ships at the refinery dock and are sampled both by the chemists and the customs inspector. The bags are then stored and emptied as needed into the raw sugar dump, whence the raw sugar is transported to the raw sugar bin of the refinery by means of bucket elevators and screw conveyers. The jute bags are given a water wash or brushed to remove the adhering sugar, dried, and sold. The wash water is evaporated to sirup, which then undergoes the usual refinery operations. Figure 2 illustrates the following sequence of *unit operations* (Op.) and *unit processes* (Pr.)[3] in the refining of cane sugar:

The first step in refining is called *affination*, wherein the raw sugar crystals are treated with a heavy sirup (60 to 70°Brix)[4] in order to remove the film of adhering molasses. This strong sirup dissolves little or none of the sugar but does soften or dissolve the coating of impurities. This operation is performed in *minglers* which are heavy scroll conveyers fitted with strong mixing flights (Op.).

The resulting sirup is removed by a centrifuge and the sugar cake is sprayed with water[5] (Op.).

The crystals are dumped into the melter, where they are dissolved in about half their weight of hot water, part of which is sweet water from the filter presses

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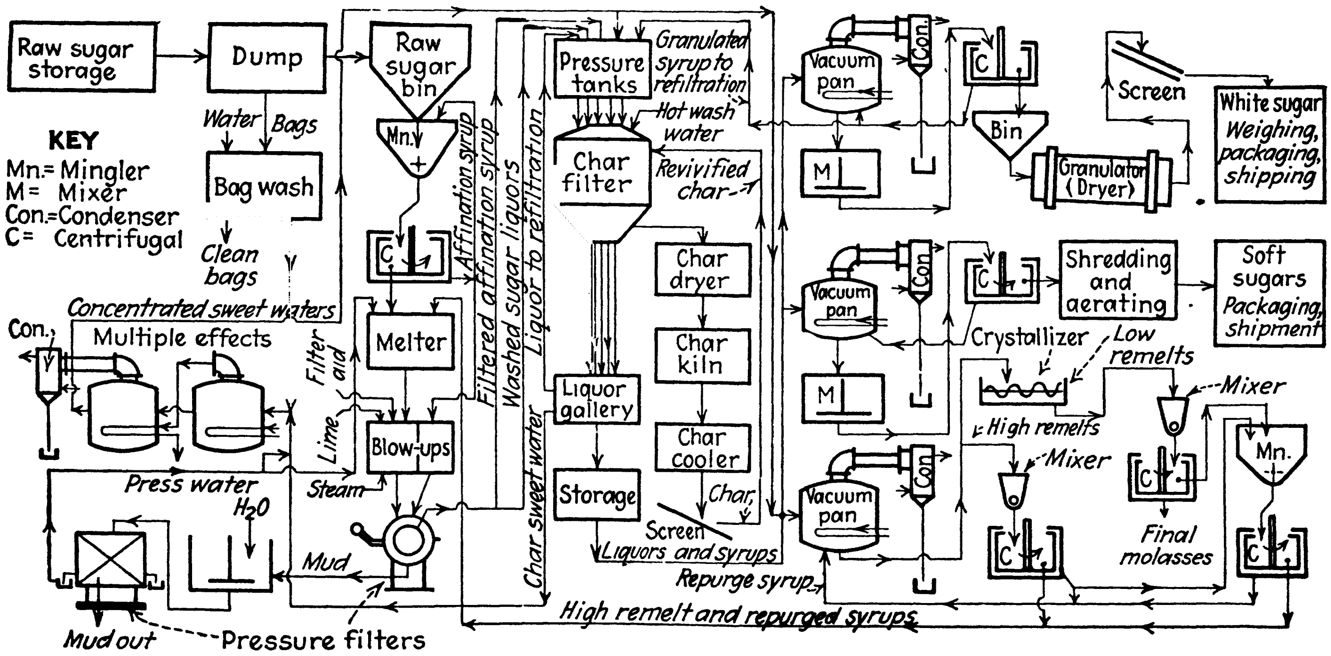
[1] For vacuum evaporation equipment and accessories, heat-transfer data, and condenser water, see section by Badger, pp. 1032–1078, in Perry, *op. cit.* On p. 1043, types of evaporators are presented, and on pp. 1068–1070 consideration is given to calculations for the economical number of effects.

[2] Analyses of molasses and how this is used for fermentation are given in Chap. XXXI. See Table 3 of that chapter.

[3] For pictured flow sheet, see *Chem. & Met. Eng.*, **47**, 119 (1940).

[4] The degree Brix is the percentage, by weight, of sucrose in a pure sugar solution; commercially it is the approximate percentage of solid matter dissolved in a liquid.

[5] Perry, *op. cit.*, pp. 1838, 1846, for centrifugals.



Raw sugar (97° Pol.)	106 lb.	Condensing water	2,000 - 3,500 lb.
Hydrated lime	0.05 lb.	Pure water	600 lb.
Kieselguhr	0.25 lb.	Process steam Power steam	175 lb.
Bone char (in process)	150 - 250 lb.	Char kiln fuel	20,000 - 25,000 B.t.u.
Bone char (revivified)	35 - 75 lb.	Employees (total)	0.3 man-hr.
Bone char (new)	0.25 - 0.3 lb.		

Per 100 lb. refined sugar (*Note: About 4lb. residual syrup also produced*)

FIG. 2.—Flow sheet for refined cane sugar.

(Op.). The sirup from the centrifugals is divided, part being diluted and reused as mingler sirup while the remainder is diluted to about 54° Brix with sweet waters and sent to the defecators.

Defecation is the preparation of the raw liquor for filtration and clarification by the addition of lime. During the operation a flocculent precipitate is formed which entangles the suspended matter and colloids; at the same time the acidity of the solution is reduced. So-called *blow-ups* (Pachuca tanks), which are circular tanks with conical bottoms fitted with steam and air connections, are used. The sirup is first neutralized with lime to a pH of 7.0 to 7.3, and diatomaceous earth is added as a filter aid (Pr. and Op.).

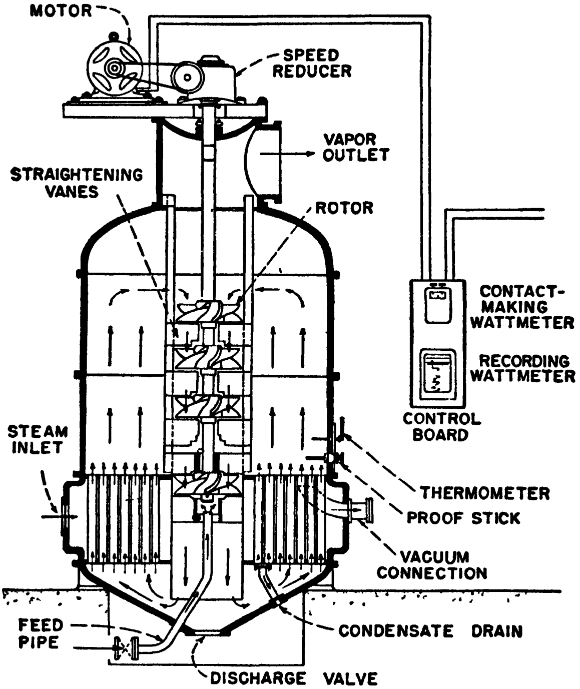


FIG. 3.—Cross section of vacuum pan equipped with mechanical circulator. The sirup is heated by passage upward through the tubes of the steam chest or "calandria" near the bottom. The liquid boils at the upper surface, vapor being drawn out through the large central pipe. A set of screw impellers forces the liquid back through the central downtake pipe. The stirrer is motor driven, with recording and controlling wattmeters in its circuit. (*Courtesy of Esterline-Angus Company.*)

The mixture is filtered and the effluent liquor from the filter presses, now free of insoluble material, still retains a large amount of dissolved impurities.[1] These impurities are removed by percolation through bone char[1] (Op.). The char tanks are about 10 ft. in diameter and 20 ft. deep. ~~From~~ 24 to 36 char filters ~~are re~~quired per 1,000,000 lb. of melt. The percolation is carried out at about 180°F. and the product is a clear, water-white sirup.

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[1] PERRY, *op. cit.*, p. 1686. Filtration and Clarification Symposia, *Ind. Eng. Chem.*, **34**, 403 (1942); RAWLINGS and SHAFOR, Ionic Exchangers: Their Applications in Cane and Beet Sugar Juice Purification, *Sugar*, **37**, No. 1, 26 (1942); TIGER and SUSSMAN, Demineralizing Solutions by a Two-step Ion Exchange Process, *Ind. Eng. Chem.*, **35**, 186 (1943).

After a certain amount of use, the char loses its decolorizing ability and must be *revivified*. This is done approximately every 90 hr. by first washing free of sugar and then removing the char and roasting it at 1000 to 2000°F. in retorts (Pr.).

The sirups from the bone-char filters are piped to the *liquor gallery* where they are graded according to purity and strength, there being four classes: 99 to 99.5 deg. purity, 90 to 93 deg. purity, 84 to 87 deg. purity, and 75 to 80 deg. purity (Op.).

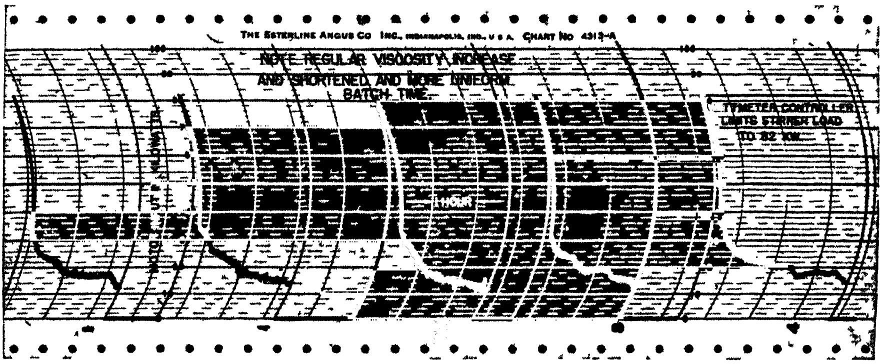

FIG. 4.—Wattmeter chart showing power input to stirrer after perfection in instrument control method. The controlling wattmeter was set to cut off the stirrer at 82 kw. Note the uniform processing time, the uniform rise in viscosity during the boiling operation, and the lack of necessity for addition of water. The average boiling time was only 2¾ hr. as compared with 4 hr. before installation of instrument control. (*Courtesy of Esterline-Angus Company.*)

The lower grades are too dark to make granulated sugar directly and are given a triple filtration and then sometimes used for soft-sugar production (Op.).

The higher grades are sent to different vacuum pans and concentrated under reduced pressure to produce various types of sugars (Op.).

Figure 3 shows a cross section of the crystallizing or "strike" vacuum pan. Here the sugar sirup is concentrated to crystallization or "seeds." These small crystals are grown to a merchantable size by a properly regulated rate of boiling or evaporation as well as of agitation. This rate should not be too rapid or new crystals (false grains) will be formed and not have time to grow, with consequent loss through the screen of the centrifugal. This operation therefore requires careful control which may be secured by charting the power consumption of the stirrer as depicted in Fig. 4.

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[1] PERRY, *op. cit.*, p. 1927; LEWIS, SQUIRES, and BROUGHTON, "Industrial Chemistry of Colloidal and Amorphous Materials," The Macmillan Company, New York, 1942.

The purest sirups are used for cubes, cut-loaf, confectioner's, and granulated sugar, and the second and third grades for "off-granulated" sugar, which is gradually mixed with the better strikes.

The pan is discharged into a mixer which keeps the whole mass from sticking together, then sent to centrifuges where the crystals are separated from the sirup, washed, and dropped to the wet sugar storage bin (Op.).

The sirup is returned to the process for further recovery of sugar (Op.).

When the purity of the sirup becomes too low, it is used for blended table sirups, with the poorer lots going for animal feed or alcohol manufacture.

The wet sugar is dried in a granulator, which is a horizontal rotating drum about 6 ft. in diameter and 25 ft. long, having a series of narrow shelves (flights) attached to its inner surface. These lift the sugar and allow it to fall through the stream of hot air flowing countercurrent to it (Op.).

The dried crystals pass over a series of screens where they are graded according to size (Op.).

Various automatic packing and weighing machines put up the sugar in barrels, sacks, and boxes (Op.).

The powdered sugars are made by grinding the granulated sugar in mills (Op.). Cube and cut-loaf sugars are prepared by mixing certain types of granulated sugar with a heavy white sirup to form a moist mass which is then molded and dried (Op.).

The soft or brown sugars are not dried but are packed directly from the centrifugals. They are graded according to color, running from No. 1 which is nearly white to No. 4 which is dark (Op.).

The yield of refined sugar obtained, based on raw sugar of 96° polarization, is usually about 93 to 94 per cent, sirup 5 per cent, with mechanical and wash losses 0.7 per cent.

In handling sugar, some inversion takes place according to the following reaction:

$$\begin{array}{lccccccc} & C_{12}H_{22}O_{11} & + & H_2O & \rightarrow & C_6H_{12}O_6 & + & C_6H_{12}O_6 \\ & \text{Sucrose} & & & & d\text{-Glucose} & & d\text{-Fructose} \\ \textit{Polarization} & +66.6^\circ & & & & +52.8^\circ & & -92.8^\circ \end{array}$$

The product is called *invert sugar*, but the polarization of the pure sucrose of +66.6° (+ to the right) now reads −20.0° (− to the left) for the resulting mixture.

$$\frac{+52.8^\circ - 92.8^\circ}{2} = -20.0^\circ$$

In recent small installations, sugar refineries have turned to processes employing activated carbon, rather than the older bone-char process.[1] The difference in the two processes lies in the purification step. The bone-char process requires a filtration of the insoluble materials in a filter followed by the decolorization in the bone-char filters. The activated carbon requires mixing tanks to mix in the activated carbon, followed by specially designed filters. The fact that the activated carbon is a much better filtering product and a much more powerful decolorizing agent than the bone char permits the substitution of one thirtieth to one fortieth of weight of bone char. There results, naturally, a saving in time, fuel, wash water, building space, and investment in equipment. In addition, the fact that the new-type plants can operate economically on a smaller scale than the old, combined with the water and fuel savings, allows these plants to be built in the tropics right alongside the raw sugar mills. This, in turn, saves on transportation and sacking of the raw sugar. This new development in sugar refining seems to be taking hold rapidly and may someday force some of the bone-char plants into obsolescence provided the cost of the decolorizing carbon can be considerably reduced. However, today, an *established* bone-char refinery can produce sugar more cheaply because the bone char can be used many times over again and reactivated at a low cost.

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[1] PERRY, *op. cit.*, pp. 1305, 1309 (flow sheet).

Manufacture of Celotex.[1]—In the United States it has been found much more profitable[2] to make insulating board from the bagasse from cane mills than to burn it under the boilers. The bagasse is baled at the raw sugar mill and shipped to the board plant. Here the bales are broken open by hand and the material conveyed by an endless belt to the rotary digesters, which are ~~14 ft.~~ in diameter. The liquor is cooked under pressure ~~in~~ order to render the fibers pliable, loosen the incrusting material, dissolve organic material, and sterilize the fiber. The resulting pulp, in a 2 to 3 per cent suspension, is pumped to swing-hammer shredders and washed in specially designed rotary washers in order to remove dirt, soluble compounds, and some pith. From the washers, the pulp enters half stock chests, where the sizing, usually papermakers' rosin and alum, is added and the mass stirred with powerful agitators to ~~remove~~ any irregularities. The fibers are refined in conical-revolving Jordans,[3] to give optimum fiber size. The refined fiber goes to stock chests, from where ~~it is~~ fed, as an approximately 2 per cent suspension, to the head box of the board machine. In the head box it is diluted to about 0.5 per cent.

The board machines, although of special design, are somewhat similar to Fourdrinier machines. The stock is fed onto forming screens, led to drying felts, and finally to press rolls. The sheets do not appear laminated but are felted together to give the required thickness. The board from these machines is 13 ft. wide, contains 50 to 55 per cent water, and is produced at the rate of 200 ft. per min. It is dried in a continuous sheet, at 300 to 450°F., in a gas- or steam-heated drier 800 to 1,000 ft. long. The product is practically bone dry and must be sprayed with water as it leaves the drier in order to bring it up to its normal water content of approximately 8 per cent. The board is now cut and fabricated into the forms in which it is used. The dust from these operations is finding use as a filler in plastics.

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[1] LATHROP, The Celotex and Cane-sugar Industries, *Ind. Eng. Chem.*, **22**, 449 (1930).

[2] The users of the bagasse pay the sugar mill enough money for it to buy other fuel.

[3] Figure 7, Chap. XXXIII.

Beet Sugar.—The familiar sugar, sucrose, can be obtained from many sources, other than cane, such as maple sirup and palm sugar. However, the great commercial sources are the sugar cane and the sugar beet. Only a skilled chemist can tell whether a sample of refined sugar originated from the tropical cane or the beet grown in the temperate zone. Ordinarily speaking, there is no distinction.

The sugar beet differs from the ordinary table beet in that it is much larger and is not red. Sugar beets are an important crop in many sections of the world, not only because of their sugar value but also because they enrich the soil for other crops. The mills begin operation in early September, the farmer harvesting his crop with machines that uproot the beets. Field workers follow the machines, remove the dirt and leaves from the beets, and load them for shipment to the factory. The beets, containing from 13 to 17 per cent sucrose and 0.8 per cent ash, enter the factory by way of flumes, small canals filled with warm water, which not only transport them but wash them as well.

Figure 5 illustrates the essential steps in the making of beet sugar. This manufacture may be divided into the following *unit operations* (Op.) and *unit processes* (Pr.):[1]

The beets are rewashed, weighed, and sliced into long narrow strips called *cossettes* (Op.).

The cossettes are dropped into large tanks or cells, 12 or 14 of which are connected in series to form a diffusion battery. The sugar is extracted countercurrently with water at 160 to 175°F., the water being in contact with each cell for 6 to 8 min. (Op.). The resulting sirup contains 10 to 12 per cent sucrose, a small amount of invert sugar, and 2 to 3 per cent ash. The pulp remaining contains 0.1 to 0.3 per cent sugar (based on the beets). This pulp is dried and sold as cattle feed (Op.).

The sirup is given a rough screening to remove foreign materials (Op.).

Milk of lime is added until the concentration is equivalent to about 2 to 3 per cent. The lime aids in the precipitation of undesirable impurities. Any calcium saccharate formed is decomposed in carbonators by passing carbon dioxide through the sirup for 10 to 15 min. The foaming that occurs at this stage is reduced by adding a small quantity of castor oil and/or tallow (Pr.).

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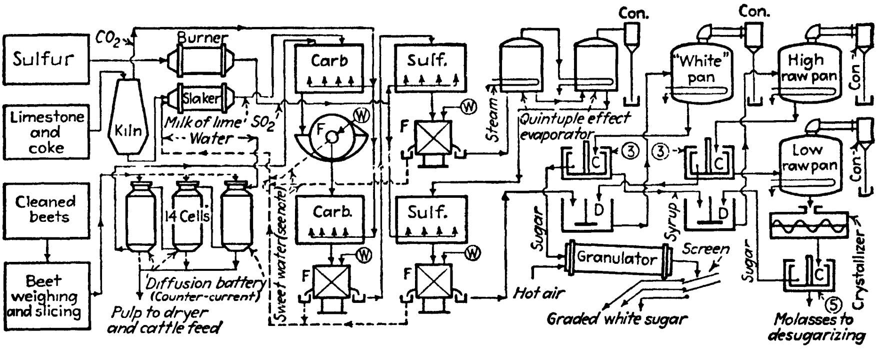
[1] See also pictured flow sheet, Beet Sugar Production, *Chem. & Met. Eng.*, **49**, No. 6, 110 (1942).

The sludge produced by the lime is equal to 4 to 5 per cent of the weight of the beets charged. This is removed by filtering the mixture on Oliver filters (Op.).

Lime is added again until the concentration is equivalent to 0.5 per cent and the mixture again carbonated, this time hot (Pr.).

It is then filtered on a plate-and-frame press (Op.).

The resulting filtrate contains a large concentration of calcium ions, which are removed by bubbling sulfur dioxide through the sirup in sulfitors. At the same time the sulfur dioxide serves to *bleach* the solution of its pale yellow color (Pr.).



Key: Carb., carbonators; Sulf., Sulfitors F., filters; W, wash water; C., centrifugals; Con., condensers; D., dissolvers

Note: About half of all plants use sweet water from filter washing for slaking lime; others use fresh water

				To Produce
Farm land	0.6 acre	Coal (power and heating)	0.66 ton	1 ton refined sugar
Sugar beets	8.0 tons	Sulfur	10 lb.	800 lb. molasses (50 per cent sucrose)
Limestone	0.5 ton	Water	90 tons	800 lb. dried pulp
Coke	0.05 ton	Direct labor	16-20 man-hr.	

FIG. 5.—Flow sheet for beet sugar.

The precipitate of calcium sulfite is removed on plate-and-frame presses (Op.).

The purified sugar is concentrated from 10 to 12 per cent sugar to about 55 per cent sugar in multiple-effect evaporators (Op.). This increases the concentration of calcium ions again and necessitates retreatment with sulfur dioxide and another filtration (Op. and Pr.).

The resulting sirup is grained in vacuum pans,[1] centrifuged, washed, dried in a granulator, screened, and packed in much the same manner as described for cane sugar (Op.).

The sirup from the first vacuum pan is given further treatment to recover more sugar crystals, but they are not pure enough for market and are sent back to the process for further purification (Op.).

The sirup remaining after the several crystallizations is called *molasses* and may be sold to the various industries as explained under Cane Sugar. Processes for the recovery of the remaining sugar have been worked out and are used commercially. Initial recovery is obtained by the Steffen process, the sirup from which may be further treated by the barium saccharate process.

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[1] McGinnis, Moore, and Alston, Low-purity Beet Sugar Factory Materials, *Ind. Eng. Chem.*, **34**, 171 (1942).

In the *Steffen process* the molasses from the centrifugals is cooled to 10°C., and finely ground quicklime added. A precipitate of tricalcium saccharate is formed and filtered off. This "saccharate cake" is washed and returned to the process, where it is mixed with the juice from the diffusion battery, thereby clarifying it in the same manner as the lime which this tricalcium saccharate partly replaced. The molasses remaining, so-called *discard molasses*, contains about 60 to 63 per cent sugar, 2 to 5 per cent raffinose, 14 to 16 per cent ash, and 1.5 to 2 per cent N_2, based on the dry material. It is sold as livestock feed. One large company is now shipping its discard molasses to a central plant for sugar recovery by the *barium saccharate* procedure.

The molasses from the Steffen process is diluted to 60° Brix and barium hydroxide solution added, precipitating the sugar as monobarium saccharate. This is separated by means of Moore leaf filters, taken up in water, and pumped into converters. In the converters it is heated to 90°F. and carbon dioxide bubbled in. Barium carbonate precipitates and is filtered off. The solution of free sugar, containing in addition some barium ions, is treated with a trace of sodium sulfate to precipitate this barium, any excess sulfate balanced with barium chloride and filtered on a plate-and-frame press. It is concentrated in vacuum pans, filtered through bone char to decolorize it, and then further concentrated until crystallization occurs. The crystals are centrifuged, washed, dried, and screened in the usual manner, resulting in a high-purity sugar. The final molasses may be reworked or sold as cattle feed, for which it is more adaptable than the molasses from the Steffen process, which contains too high a percentage of nitrogen.

The process[1] is dependent upon the conversion of the barium carbonate obtained into the hydroxide which is the precipitating agent. This is accomplished by mixing the carbonate with silica and/or monobarium silicate from previous runs in sufficient proportions to form dibarium silicate, adding coke, and charging into a rotary kiln, fired by natural gas.

$$2BaCO_3 + SiO_2 \rightarrow 2BaO{\cdot}SiO_2 + 2CO_2$$
$$BaCO_3 + BaO{\cdot}SiO_2 \rightarrow 2BaO{\cdot}SiO_2 + CO_2$$
$$2BaO{\cdot}SiO_2 + H_2O \rightarrow BaO{\cdot}SiO_2 + Ba(OH)_2$$

The temperatures employed are somewhat lower than 2400°F. The clinkers obtained drop out of the end of the furnace and are crushed and leached in a Dorr thickener. The hot water converts the dibarium silicate into monobarium silicate and a solution of barium hydroxide which is filtered and cooled, precipitating barium hydroxide. The monobarium silicate sludge is pumped over a large Oliver filter and returned to the furnace, where it is mixed with additional barium carbonate for conversion. From time to time, it is necessary to add fresh barium oxide to compensate for the slight loss that occurs, owing to lack of complete conversion of the monobarium silicate. It is this latter fact which makes the process somewhat costly, since the barium compounds added must be quite pure.

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[1] DEGUIDE, "Process for Obtaining Barium Hydrate," U.S. Pat., 1247510, Nov. 20, 1917.

Energy Requirements.—In the direct manufacture of sugar there are few or no chemical changes that require energy. Almost all the steps in the manufacturing sequences involve physical changes or unit operations. These consume energy in the form of *power* for crushing, pumping, and centrifugation, and *heat* for solution, evaporation, and drying. On the bottom of the flow sheets for refined cane sugar and for beet sugar (Figs. 2 and 5) are given some average figures for energy material (steam or coal) requirements. The steady improvement by chemical engineers of the equipment necessary to make these various unit operations function efficiently has gradually reduced the energy requirements to the reasonable amounts given.

In the raw cane-sugar mills, fuel for producing sufficient steam for power and heat comes from the burning in special boilers of the bagasse or waste from sugar extraction. In the United States, some bagasse is turned into Celotex (see page 629). Consequently other fuel must be employed.

In all sugar-manufacturing establishments, there is an economical dual use of steam (see Chap. V) wherein high-pressure steam from the boiler is expanded through a reciprocating engine or a turbine to furnish power and wherein the exhaust steam is condensed to secure heat for evaporation of the juices and sirups. The condensed steam resulting is pumped back to the boilers or is employed for making sirups.

In beet-sugar refining, Fig. 5 indicates 0.66 ton of coal for 1 ton of refined sugar or 10,000 B.t.u.[1] per lb. of sugar. Some plants now produce 1 lb. of refined beet sugar with only 6,000 B.t.u.[2]

Miscellaneous Sugars.—Lactose or milk sugar is presented in Chap. XXXIX under Milk Chemicals, while sorbitol and mannitol are included in Chap. XVI on Electrolytic Industries. Much molasses serves as the carbohydrate raw material in the fermentation industries (Chap. XXXI) while any excess molasses is consumed as cattle feed.

STARCHES AND RELATED PRODUCTS

Although starch is known to have the approximate formula $(C_6H_{10}O_5)_n$, its exact structure is still unsolved. It may be regarded as a chain polyglucosidic macromolecule. It is one of the most common substances existing in nature and is the major basic constituent of the average diet. Industrially, its applications are numerous, being used in more than 300 modern industries, including the manufacture of textiles, paper, adhesives, insecticides, paints, soaps, explosives, and such derivatives as dextrins, nitro-starch, and corn sugar. Starch has been the object of a large amount of research in recent years, covering such products as heat-resistant adhesives, esters comparable to the cellulose esters, oxidation of dextrose to carboxylic acids, and the preparation of wetting agents.

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[1] PERRY, *op. cit.*, p. 2350, for B.t.u. in typical coals.

[2] SHAFOR, Process Economy in Beet Sugar, *Chem. & Met. Eng.*, **47**, 464–467 (1940).

Historical.[1]—It is a well-known fact that the ancients used starch in manufacturing paper (as an adhesive and stiffener) as early as 3500 B.C. The Egyptians of this period cemented papyrus together in this manner. Between A.D. 700 and 1300 most paper was heavily coated with starch but the practice was abandoned toward the end of the fourteenth century and was not revived until our modern era. The use of starch in textiles began during the Middle Ages, when it was very common as a stiffening agent. By 1744 the English were using it in sizing and warp glazing.

Textile demands soon brought about the introduction of potato starch to supplement the wheat starch solely available up to this time. In 1811 the discoveries of Kirchhoff with respect to glucose and the thinning of starches by enzymatic action gave great impetus to starch manufacture through the increased fields of application which they created. The use of roasted starch did not begin until 1821, its usefulness being discovered as the result of a textile fire at Dublin, Ireland. It had, however, been prepared by LeGrange as early as 1804.

The first starch produced in this country was white-potato starch, made at Antrim, N. H., in 1831. In 1842, Kingsford began the production of corn starch, which became increasingly popular until by 1885 it had risen to the position of the leading textile starch in the field. It was in this period also that the manufacture of dextrins (roasted starches) was begun in the United States.

Sweet-potato starch has been made in Japan for many years, but its manufacture in the United States was not undertaken until 1934. By 1939, however, production had risen to 2,700,000 lb. White-potato starch is quite common in Germany, where over 250,000,000 lb. are produced each year. Even in the United States it is still second only to corn starch production.

Uses and Economics.—In 1939 there were about 2.7 billion pounds of starch produced in the United States for all purposes, including conversion into sirup and sugar. Of this total, 2,684,000,000 lb., or over 99 per cent, was corn starch. The actual production of starch and its various products is given in Table 3. Imports during the same period, consisting principally of tapioca and sago starches, totaled 429,000,000 lb., and exports, principally corn starch, totaled 201,000,000 lb.

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[1] RADLEY, "Starch and Its Derivatives," D. Van Nostrand Company, Inc., New York, 1940.

The largest single use for *corn starch* is as a food, 250,000,000 lb. a year being consumed in this way. Industrially, the largest consumer is the cotton textile industry which uses more than 100,000,000 lb. a year.[1] A close second is the laundry trade (domestic and commercial) which requires a similar amount. The third largest industrial consumer is the paper industry which needs more than 70,000,000 lb. of corn starch a year as filler and sizing material. Following it is the explosives industry which employs large amounts in the manufacture of explosives. Other industrial uses include the manufacture of paints, insecticides, soap, pharmaceuticals, fuel briquettes, battery compounds, adhesives, and rubber goods.[2]

Potato starch can be employed for almost every one of the uses outlined for corn starch. It has the advantage of a large granule size and more desirable phosphoric acid content. *Wheat, rice, arrowroot,* and *cassava (tapioca) starches* also have many of the same applications as corn starch.

TABLE 3.—UNITED STATES PRODUCTION OF STARCH, CORN SIRUP, CORN SUGAR, CORN OIL, AND DEXTRIN IN 1939[a]

	Pounds
Starch:	
Corn	1,120,264,541
Potato	22,187,000
Wheat, rice, and processed	70,381,486
Corn sirup:	
Unmixed	957,297,004
Mixed	273,885,459
Corn sugar	467,153,433
Dextrin	106,477,418
Corn oil:	
Crude	63,385,966
Refined	104,039,977
Corn-oil cake and meal	65,140,000

[a] 1939 Census of Manufactures.

Rice starch is particularly preferred for laundry purposes. Tapioca starch is very common as a food.

In addition to the starches themselves, there are made many further reaction products. These include the following: *Dextrin,* or "roasted starch," which is available in more than 100 different blends and types, varying from pure white to light yellow in color; they are used to make a great number of different pastes, gums, and adhesives. *Corn sirup* is a combination of dextrose, maltose, dextrin, and water. Approximately a billion pounds a year are used as a food, in the manufacture of candies, to regulate texture in textile manufacture, in the preparation of tobacco, in paper manufacture, and in tanning. *Corn sugar*, or dextrose, is the sugar found in the blood. It has many food uses dependent upon its lower rate of crystallization, lesser sweetness, and different crystal formation. It is widely employed by the medical profession. Industrially, it is important as a constituent of the viscose-rayon spinning bath, as a source of lactic acid by fermentation, and in the brewing and tanning industries.[1]

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[1] MORGAN, Textile Starches, *Am. Dyestuff Rptr.*, **29**, 494 (1940).

[2] NEWKIRK, Industrial Use of Starch Products, *Ind. Eng. Chem.*, **31**, 153 (1939).

Manufacture of Starch, Dextrin, and Dextrose from Corn.—Corn refining is an enormous industry, consuming 60,000,000 to 80,000,000 bu. of corn every year, and at one time as high as 100,000,000.

Chemically, the corn kernel consists of from 11 to 20 per cent water and the following nonaqueous constituents:[2]

	Per Cent
Starch	60.0–65.0
Proteins	8.0–10.0
Pentosans	7.0– 7.5
Oil	3.0– 4.5
Fiber	1.2– 1.5
Ash	1.2– 1.3

On this basis, 1 bu. of corn yields about 32 lb. of starch, 21 lb. of by-products (gluten meal, corn bran, germ oil meal, and steep water), and 1.5 lb. of corn oil.

The sulfurous acid method of refining is employed, using shelled corn as raw material[3] and the following *physical changes* or *unit operations* (see Fig. 6). The first operation consists of cleaning the corn by means of screens, compressed air, and electromagnets. The cleaned corn is steeped for 30 to 40 hr. in warm water (115 to 125°F.) containing about 0.30 per cent sulfur dioxide. The latter prevents fermentation during the soaking period. Large, hopper-bottomed steeping vats are employed for this operation which softens the gluten and loosens the hull. The steep water dissolves salts, soluble carbohydrates, and protein. It is evaporated to 18°Bé. and sprayed over the gluten feed obtained later in order to increase the nutritive value of the feed. The steep-water evaporated product is now widely employed in the growing of penicillin (Chap. XXXI).

The softened kernels are ground in Fuss mills (also known as *attrition* mills) which consist essentially of two vertical, rotating plates with pro-

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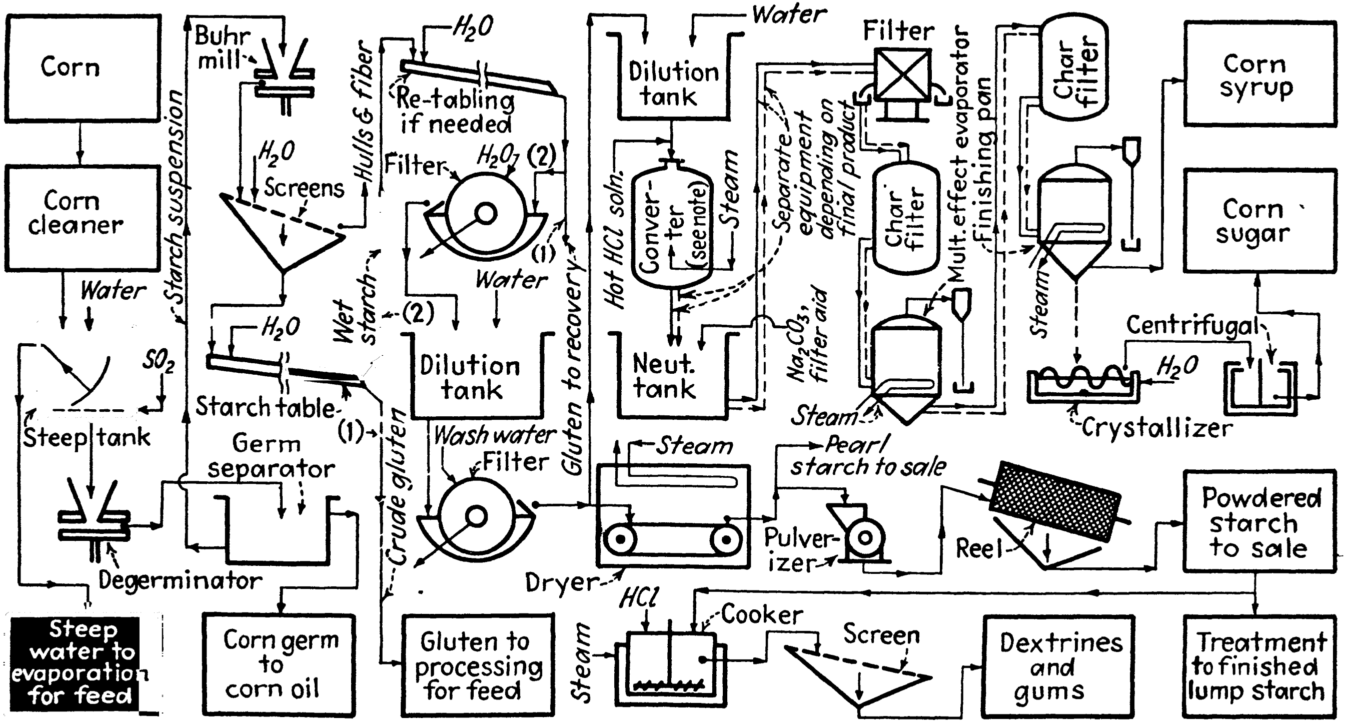
[1] NEWKIRK, Development and Production of Anhydrous Dextrose, *Ind. Eng. Chem.*, **28**, 760 (1936).

[2] WALTON, "A Comprehensive Study of Starch Chemistry," Vol. I, pp. 130–139, Reinhold Publishing Corporation, New York, 1928.

[3] WILLIAMS, Maize Starch, *Ind. Chemist*, **9**, 129 (1933).



Note: Degree of hydrolysis controllable by time, temperature and concentration in converter, thus permitting different end products, such as sugars or syrups

FIG. 6.—Corn products flow sheet.

jecting studs, which crack the grain but do not injure the germ. The latter is liquid-separated from the hull in so-called *germ separators* which are large agitated tanks. The germ, because of its oil content, is floated away from the rest of the kernel and skimmed off. It is washed, dried, ground, and put through expellers (see Chap. XXVIII).

The remainder of the corn kernel contains the starch, gluten, and cellulose. It is wet-ground in buhrstone mills and passed through a series of hexagonal reels open at both ends and covered with silk bolting cloth. Water washes the starch and gluten through the silk sides while the hull and fiber particles tumble out the lower end. The last bits of hull and fiber are removed on rectangular shaker screens covered with silk bolting cloth, after which the starch-gluten suspension flows onto the starch tables.

Starch tables are flat-bottomed troughs about 2 ft. wide, 10 in. deep, and 100 to 130 ft. long. The lower end is 3 to 4 in. lower than the head end. The starch-gluten suspension, concentration 6 to 7°Bé., flows slowly down the tables, the heavier starch granules gradually settling to the bottom and the gluten suspension flowing off the lower end. The gluten is removed by coagulation with acid (0.3 per cent) and settling. It is centrifuged, filtered, admixed with the fibers and hulls from the reels and shakers, sprayed with concentrated steep water from initial treatment, and dried to produce corn gluten feed. The gluten water from the settling tanks is returned to the steeping vats.

When 8 in. or more of starch have deposited on the tables, flow is stopped and the starch flushed off the tables. The resulting suspension is sent to rotary filters, where the starch is washed and partly dried. If a particularly pure starch is being prepared, it is necessary to retable the suspension at this point. The wet or "green" starch obtained at this point contains approximately 45 per cent water and is ready for further drying to commercial starch, or additional processing to dextrin, sirup, or sugar.

If *commercial starch* is to be made, the wet starch is dried in kilns or drying tunnels. The time and temperature vary with the type of product desired, *i.e.*, pearl starch, crystal starch, powdered starch, and lump starch. Soluble starches, thin boiling starches, thick boiling starches, and purified starches are made by additional special treatment with alkali or acid.

Another product of corn refining is *dextrin*, or "roasted starch." Starch itself is not soluble in water, but its derivative, dextrin, dissolves readily to give various commercial adhesives, pastes, and gums. Conversion is carried out in round metal tanks equipped with a scraper and open at the top. The scraper prevents sticking during the heating period which may vary from 2 hr. for some white dextrins to 15 hr. for certain

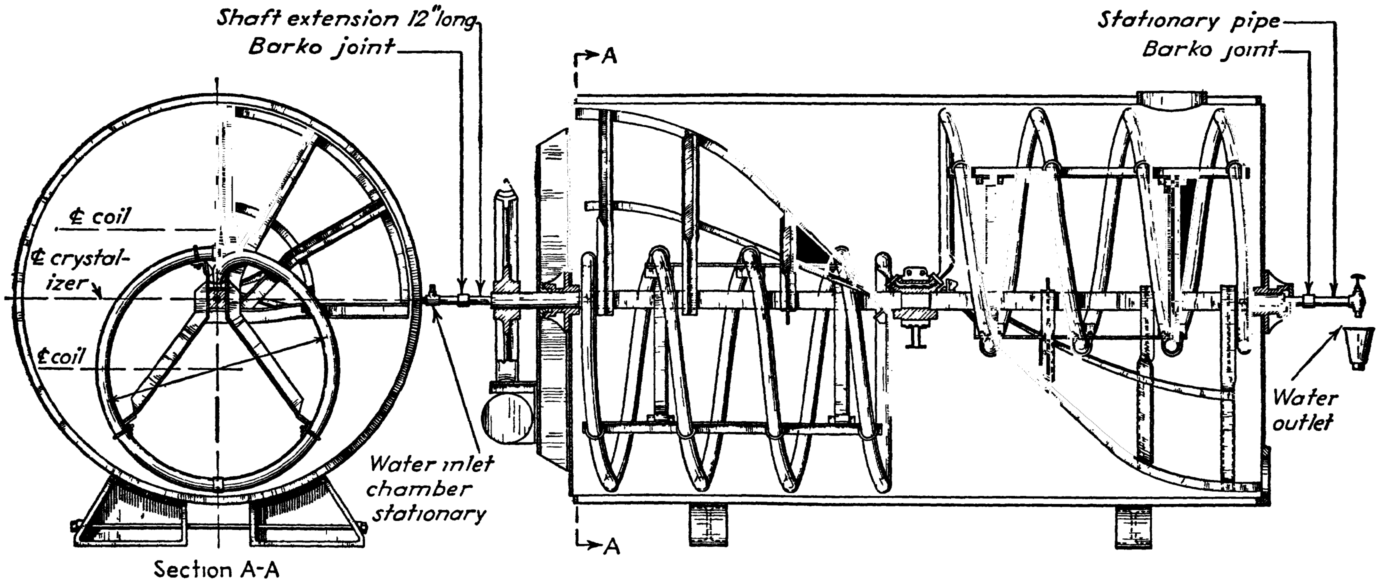


FIG 7—Sugar crystallizer provided with scraper and eccentric coil crystallizer Such cooling with stirring improves heat transfer while maintaining uniformity in temperature drop Rotation $\frac{1}{8}$ r p m Crystallization time is about 100 hr for dextrose Water is passed through coil for cooling. (*Courtesy of Kilby Manufacturing Company*)

gums. The temperature also influences the kind of dextrin being prepared (see Fig. 6).

When starch is *hydrolyzed* in the presence of acid, the product is either *corn sirup* or *corn sugar* (dextrose), depending upon the extent of the conversion. Hydrochloric acid is the hydrolyzing agent employed almost exclusively in the United States and sulfuric acid in Europe. A green starch suspension is pumped into a cylindrical copper converter and heated to 270 to 280°F. over a period of 15 to 20 min. If corn sugar (dextrose) is being prepared instead of the sirup, a slightly stronger acid (0.2 per cent) and a longer conversion period are necessary. The converter mixture is adjusted to a pH of 4.5 to 5.5 with soda ash, filtered, and concentrated to 30°Bé. The resulting sirupy liquid is decolorized with animal charcoal and evaporation continued, now under vacuum, until the concentration has reached 42 to 45°Bé. The resulting sirup, containing dextrose, maltose, dextrin, and water, is cooled, packaged, and sold as corn sirup or glucose. If pure corn sugar is desired, the hydrolysis is carried farther so that little or no starch and dextrin are in the sirup. This sirup, concentrated to 42°Bé., containing about 80 per cent corn sugar, is cooled, seeded, and crystallized slowly with gentle agitation in closed horizontal cylindrical vessels over 100 hr. (see Fig. 7). This sugar is separated from its mother liquor in centrifuges, washed, and dried. Three types of corn sugar, known as crude, pressed, and refined, are available. The commercial product is usually sold as dextrose or corn sugar but chemically this is the monosaccharide *d*-glucose.

MISCELLANEOUS STARCHES

There are two varieties of potato starch manufactured at present: white-potato starch and sweet-potato starch.

White-potato Starch.[1]—White potatoes contain 10 to 30 per cent starch. Upon being received at the factory, they are washed and disintegrated in a rasping machine to a watery pulp. The pulp is treated with sulfur dioxide gas, in the ratio 0.5 lb. per lb. of starch and sent to a continuous horizontal centrifuge with an imperforate conical bowl and continuous spiral ribbon starch remover. The protein water mixture is separated from the starch, cellulose, and skins, and the latter resuspended in water as a milk. The suspension is sieved, the pulp from the sieves is reground and resieved. The milk from the second sieving is again passed through a centrifuge, suspended in water, and sent to the tables for separation. From this point on operations are similar to those used for the manufacture of corn starch.

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[1] BRAUTLECHT, Manufacture of White Potato Starch in the United States, *Ind. Eng. Chem.*, **32**, 893 (1940).

Sweet-potato Starch.—Sweet potatoes contain an average of about 24 per cent starch.[1] The potatoes are washed, crushed in a hammer mill, mixed with a saturated calcium hydroxide solution, and sent to shaker screens where the starch is set free. The pulp from the screens is reground and sent through the entire cycle once more. The starch liquor obtained from these operations is screened to remove fibers, adjusted to 5°Bé., and tabled. The resulting product must be retabled and rescreened. It is bleached for 2 hr. with sodium hypochlorite, the excess chlorine removed with sulfur dioxide, and the liquor centrifuged. The resulting starch is dried under vacuum.

Wheat Starch.[2]—In the manufacture of this cereal starch, the major difficulty encountered is the separation of the starch and gluten. This may be accomplished by fermentation or Martin's process. In the fermentation process the grain is steeped until soft, a mash made which is left to ferment for 7 to 30 days. The gluten is solubilized, and the remainder of the grain loses its adhesive properties. At the proper point the starch is washed from the mixture in a washing drum. The process is not used extensively because of its objectionable odor, low yield, and wastage of gluten. In the Martin process, wheat is ground to flour, made into a dough with about 40 per cent of its weight of water and stored for 1 hr. The resulting mass is divided into small lumps and placed in a semicircular sieve where a traveling roller presses out the starch, which is removed by a fine water spray. The resulting liquor is treated in much the same manner as corn starch liquor.

Rice Starch.—This is made from "cargo rice" which still has the brown, outer cuticle attached, or from the broken white grains rejected as foodstuff. The rice is steeped for 24 hr. with caustic soda solution (specific gravity 1.005) in cement or iron tanks with perforated false bottoms. At the end of the period the liquor is withdrawn, the rice washed, fresh liquor added, and steeping continued for another 36 to 48 hr. The resulting softened grains are ground with a caustic solution to a specific gravity of 1.24 and the mash is centrifuged. The solids obtained include all sorts of fibrous material, starch, and gluten. These are resuspended, a small amount of formaldehyde is added to inhibit fermentation, and they are recentrifuged and washed. A bleaching or bluing agent may be added at this point. The liquor is screened, adjusted to a specific gravity of 1.21, and sent to draining boxes having perforated bottoms covered with cotton fabric. Settling is aided by applying suction through the box bottom. The resulting starch blocks are cut and placed on porous plates in a crusting stove, where they are allowed to dry for 2 days at 50 to 60°C.

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[1] PAINE, Manufacture of Sweet Potato Starch in the United States, *Ind. Eng. Chem.*, **30,** 1331 (1938).

[2] RADLEY, *op. cit.*

Cassava (Tapioca) Starch.—This starch is obtained from the roots and tubers of the manioc plant, which grows in the East Indies, West Indies, and South America. The average starch content varies from 20 to 30 per cent. In general, the roots are pulped and washed on sieves to obtain the starch. In the West Indies, the pulp is squeezed through coarse bags to expel the starch milk. Separating and purifying operations are similar to those described for potato starch.

Sago Starch.—This is obtained from the pith of the sago palm, and also from yams in the East Indies and Borneo. Pearl sago starch is made by drying the starch so as to form a plastic dough, which is then forced through sieves and dried in the air.

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CHAPTER XXXI

FERMENTATION INDUSTRIES

The employment of microorganisms to convert one substance into another is a science that man is assiduously studying and is energetically applying. Although the fermentation of fruits to alcohol was known to primitive man and although the making of various beverages out of fruits and grains has been well established for centuries, it is only during the past generation that the wider application of this procedure has been recognized. Now, man is directing the life processes of yeasts, bacteria, and molds to the production of chemicals. Alcohol can be viewed as having been produced in this way from the earliest times, but the making of acetone and butanol, of acetic acid, lactic acid, citric acid, and penicillin is a recent technical accomplishment.

The foundation of the scientific understanding of fermentation, indeed of the action of all microorganisms and hence of their economic control, rests firmly upon the genius of one man, Louis Pasteur. He showed that fermentation is directly caused by the life processes of minute organisms. By understanding how these microorganisms function and by the recognition that varieties of yeasts, for instance, act differently and that environment fundamentally affects even a given strain, one can control these processes of fermentation in an exact scientific manner.

The fungi are a branch of the nongreen plants and include yeasts, molds, and mushrooms. These feed upon organic materials. It is this feeding that interests the manufacturer; for if he supplies to certain yeasts, bacteria, or molds the necessary fundamental energy food, together with the other needed nutrients, then these microvegetative organisms will not only grow and multiply but will change the food into other chemical substances.

Yeasts and bacteria are unicellular and of very small dimensions. The yeasts are irregularly oval and perhaps 0.004 to 0.010 mm. in diameter. The bacteria are smaller, mostly less than 0.007 mm. in the longer dimension and more diverse in shape. Many of them, the bacilli, are rod-shaped. The yeasts multiply by budding, and the bacteria by binary fission. The molds are multicellular filaments and increase by vegetative growth of the filament. Sporulation provides for the next cycle, as it does also with many bacteria. The vegetative reproduction cycle of these bacteria and of the yeasts is short—measured in minutes. Because of this, they multiply exceedingly fast.

Many microorganisms have been brought into useful service to man. One of the striking developments in the past 25 years has been the extension to the making of chemicals, other than alcohol, of the life processes of these minute vegetative organisms. Table 1 lists some of these performances, which, in larger industrial scale, embrace the manufacture of acetone, butanol, acetic acid, lactic acid, and citric acid. This table shows the importance of fermentation in foods. Recently several of the older laboratory procedures, such as the making of citric and gluconic acids, have been developed to the industrial stage. One of the most striking wartime developments is that of penicillin from the mold *Penicillium notatum*. These fermentation processes are frequently in direct competition with strictly chemical syntheses. Even alcohol by fermentation has an active competitor in alcohol from the ethylene of the petroleum-cracking stills, and fermentation acetic acid must meet acetic acid from acetylene.

By fermentation under controlled conditions, many *unit processes* are carried on in our factories. Among these the following are important: *Oxidation, e.g.,* alcohol to acetic acid, sucrose to citric acid, and dextrose to gluconic acid. *Reduction, e.g.,* aldehydes to alcohols, as acetaldehyde to ethyl alcohol and sulfur to hydrogen sulfide. *Hydrolysis, e.g.,* starch to glucose or sucrose to glucose and fructose. *Esterification, e.g.,* hexose phosphate from hexose and phosphoric acid.

However, many of the chemical reactions caused by microorganisms or their enzymes are very complex and cannot be easily classified by a principal unit process, as for instance the formation of acetone, butanol, and alcohol by members of the *Clostridium* genus acting on carbohydrates, as depicted in Fig. 7, or even the formation of alcohol from glucose.

In understanding, and hence in correctly handling these microorganisms, a sharp differentiation should be made usually between the initial increase to a sufficient quantity of a selected strain of these organisms and their subsequent processes whereby, either through their continued *living* or as a result of *enzymes* previously secreted, the desired chemical is manufactured. To get a maximum chemical yield it is frequently advisable to suppress additional increase in quantity of the microorganism. Highly specialized mycologists[1] working in well-equipped laboratories are engaged in selecting and growing the particular strain of the organism that experiment has shown to produce the chemical or chemicals wanted, and with the *greatest yields* and the *least by-product.* To do this, it is necessary to study the time of fermentation, as well as the type and the concentration of the substrate. No longer will just any yeast do to make industrial alcohol or a fermented beverage; not only are wild yeasts excluded, but a special strain must be used. Competitive industry demands the best conversion of the raw materials (food of the microorganisms) to the product wanted and, furthermore, with the necessary quality. This all necessitates a great amount of original work and continuous careful control, to ensure economic success. In the first place, after the desired strain has been found and isolated, it should be preserved uncontaminated in its cyclic growth in the laboratory, so that this same strain can be used daily to start the industrial process.

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[1] Those skilled in dealing with bacteria, yeasts, and molds. Industrially, one laboratory will frequently control the use of only one species of bacteria, for example.

TABLE 1.—SURVEY OF IMPORTANT FERMENTATIONS[a]

Food	Industrial	Laboratory
Bread (*Y.*)[b]	Alcohol (*Y.*)	Succinic acid (*M.*, *Y.*, and *B.*)
Cheese (*M.* or *B.*)	Yeast (*Y.*)	Fumaric acid (*M.*)
	Enzymes[c] (*M.*, *Y.*, and *B.*)	
Vinegar (*B.* and *Y.*)	Carbon dioxide (*Y.*)	Kojic acid (*M.*)
Sauerkraut (*B.*)	Lactic acid (*B.*)	Butyric acid (*B.*)
Koji (*M.* and *Y.*)	Gallic acid (*M.*)	Propionic acid (*B.*)
Tea (*B.*)	Glycerine (*Y.*)	Malic acid (*M.* and *Y.*)
Coffee (*M.*)	Acetic acid (*B.*)	Fuel gas, H_2 (*B.*)
Cocoa (*B.* and *Y.*)	Acetone-butyl alcohol (*B.*)	Dihydroxy-acetone (*B.*)
Pickles (*B.*)	Citric acid (*M.*)	Acetic acid from cellulose (*B.*)
Olives (*B.*)	Gluconic acid (*M.*)	
Yeast (*Y.*)	Penicillin (*M.*)	
Vitamins (*B.* and *Y.*)	Sulfuric acid from sulfur (*B.*)	
Beer (*Y.*)	Precipitation iron (*B.*)	
Wine (*Y.*)	Nitrogen fixation (*B.*)	
Whisky (*Y.*)	Fusel oil (*Y.*)	

[a] After HERRICK, Some Industrial Fermentations, *Chem. Bull.* (*Chicago*), **18**, 35 (February, 1931). *Cf.* the important article by May and Herrick, Production of Organic Acids from Carbohydrates by Fermentation, *U.S. Dept. Agr. Circ.* 216 (May, 1932).

[b] *Y.* stands for yeast; *B.* for bacteria; *M.* for molds.

[c] WALLERSTEIN, Enzyme Preparation from Microorganisms, *Ind. Eng. Chem.*, **31**, 1218 (1939).

The yeasts, bacteria, and molds employed require specific environments and foods to ensure their activities. The concentration of the sugar or other food affects the product. The temperature most favorable varies (5 to 40°C.). The pH also has great influence. Indeed, the bacteriologist has developed some acid-loving yeasts, so that the *wild yeasts*, not liking this condition, do not flourish. Some microorganisms require air (aerobic), and others go through their life processes without air (anaerobic). Certain anaerobes will neither grow nor function in the presence of air. In directing these minute vegetative organisms, conditions can be controlled to encourage the multiplication of the organism first and then its functioning either directly or through the enzymes secreted. How important this is can be seen from the knowledge that to grow 1 g. of yeast (dry basis) requires 1.5 to 2.0 g. of monosaccharide per day, and 6 g. to maintain the yeast. By virtue of this growth organic catalysts or enzymes are formed frequently that directly cause the desired chemical change. During the growth period, in addition to the primary or energy food, such as monosaccharides for yeast, there are needed various nutrients, such as small amounts of phosphates, nitrogenous compounds, as well as the favorable pH and temperature. Finally, certain substances will poison these useful little vegetables and their enzymes. Even the alcohol formed by the yeasts will eventually reach a concentration (varying with the yeast from about 2 to 15 per cent) that will suppress the activity of the organism and of the enzymes. We are, furthermore, recognizing the importance of the life processes of the microorganisms, in making vitamins, some of which are being recovered and sold in a concentrated form.

Is not this story somewhat akin to what happens in the world in which we live with its trees and animals, yes, and man himself?

INDUSTRIAL ALCOHOL

Industrial alcohol was an outgrowth of alcoholic beverages, but it has become important in its own right by virtue of its economically useful properties as a solvent and for synthesis of other chemicals. Alcohol is sold as tax-paid[1] alcohol or, much more widely, as nontaxed denatured alcohol. There are two classes of the latter: completely denatured and specially denatured alcohol. The *completely denatured* formulas comprise admixtures of substances which are difficult to separate from the alcohol and which smell and taste badly—this all being designed to render the alcohol nonpotable (not fit for a beverage). Such completely denatured alcohol is sold widely without bond. The public uses it as an antifreeze, and the factories find it an essential raw material.

Over 98 per cent of the total domestic withdrawals for sale of completely denatured alcohol embrace Formulas[2] 13 and 14, with gallonage of 9,346,455 and 5,863,036 wine gallons, respectively, for the fiscal year 1940, and of 13,304,098 and 4,160,584 wine gallons for the fiscal year 1941.

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[1] Federal tax of $3 per proof gallon, equivalent to $5.70 per wine gallon of 190-proof, or 95 per cent alcohol by volume. This was increased to $9 per proof gallon by 1944. To this the states may add their own tax. The total sum collected by the Federal Alcohol Tax Unit was $1,423,646,456 during the fiscal year 1943. This was largely on beverages.

[2] See footnote 1 on p. 647.

FORMULA No. 13

To every 100 gal. of ethyl alcohol of not less than 160 deg. proof add
- 4 gal. of ST-115 or a compound similar thereto.[1]
- 2 gal. of methyl isobutyl ketone.
- 1 gal. of gasoline.
- 0.5 gal. of Agdite or a compound similar thereto,[1] or 1 gal. of Hydronol or a compound similar thereto.

FORMULA No. 14

To every 100 gal. of ethyl alcohol of not less than 160 deg. proof add
- 5 gal. of FD-13 or a product similar thereto.[1]
- 2.25 gal. of methyl isobutyl ketone.

The Federal government has recognized the needs of industry for alcohol in such form that it can enter into specialized manufacturing processes where the denaturants used in the completely denatured alcohols would interfere. So, in the years that have elapsed since 1906, when the first United States denatured alcohol law was passed, many formulas, particularly of *specially denatured alcohol,* have been tested and approved by the Federal authorities. Such special formulas are limited in their use to certain designated processes and are manufactured, stored, and used under bond, to ensure such specially denatured alcohols from unlawful consumption. However, the 55 approved special formulas under their authorized uses enter into an exceedingly broad section of the entire industrial life of the nation, and total 111,509,432 and 136,319,810 wine gallons for withdrawals during the fiscal years 1940 and 1941. Typical specially denatured formulas[2] are

To every 100 gal. of ethyl alcohol, add for the designated number:
- No. 1. 5 gal. of approved wood alcohol.
  - Withdrawals for 1940: 31,019,934 wine gallons; 1941: 35,216,087 wine gallons.
  - Authorized uses: lacquers and other surface coatings, polishes, dyes, perfumes, chemicals, etc.
- No. 2B. One-half gallon benzol.
  - Withdrawals for 1940: 25,415,813 wine gallons; 1941: 37,651,823 wine gallons.
  - Authorized uses: plastics, dehydrations, explosives, food products, dyes, chemicals, etc.

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[1] The denaturants added to make completely denatured alcohol are frequently commercial mixtures. Full specifications for such are given in the pamphlet entitled "Formulae for Completely and Specially Denatured Alcohol," published by U.S. Bureau of Internal Revenue as appendix to Regulation 3, 1939. ST-115 is an impure pyroligneous product, free from wood alcohol but produced from destructive distillation of wood. Agdite is a compound petroleum product. Hydronol and FD-13 are organic hydrogenated products of specified properties as to boiling range and with characteristic taste and odor.

[2] Formulas 1, 2B, and 29 accounted for 77.4 per cent of the withdrawals during the fiscal year 1941.

No. 29. One gallon of 100 per cent acetaldehyde.
Withdrawals for 1940: 27,418,710 wine gallons; 1941: 32,582,732 wine gallons.
Authorized uses: manufacturing acetaldehyde, acetic acid, ethers, esters, etc.
No. 40. Three ounces of brucine and ⅛ gal. of tertiary butyl alcohol.
Withdrawals for 1940: 2,613,965 wine gallons; 1941: 3,145,278 wine gallons.
Authorized uses: toilet preparations, hair and scalp lotions, deodorants, toilet waters, lotions, soaps, bath salts, etc.

In industrial nomenclature *alcohol* means ethyl alcohol or ethanol with the formula C_2H_5OH. It is sold by the gallon which weighs 6.794 lb. and contains 95 per cent C_2H_5OH and 5 per cent H_2O both by volume and at 15.56°C.[1]

Industrial Applications.—No distinction is made as to the source of the alcohol, whether it be from fermentation or from the rapidly increasing synthesis from ethylene from petroleum. For tax purposes a *proof gallon* is used, which signifies a gallon containing 50 per cent alcohol by volume.[2] It is interesting to observe that this is about the lower limit of burning for alcohol dilutions by direct ignition at ordinary temperatures. Ordinary alcohol of 95 per cent strength is thus 190-proof alcohol, and pure anhydrous alcohol is 200 proof.

Uses and Economics.—Tax-paid pure alcohol is used only for medicinal, pharmaceutical, flavoring, or beverage purposes. The large consumption and the wide field of industrial application have arisen only since the availability of the low-priced tax-free denatured alcohols. The largest direct-consumer use is as an antifreeze, followed as a solvent in surface coatings and cosmetics, and as a dehydrating and moistening agent in various nitrated celluloses. Alcohol enters into further reactions in large quantities to furnish a great number of derivatives, among which can be named ethyl acetate and many other ethyl esters, acetaldehyde, acetic acid, and ethyl ether.

In petroleum-poor countries it is economical to mix alcohol (frequently absolute) in with the gasoline in order to conserve the petroleum products. For such mixtures, if the alcohol is not anhydrous, a blending agent is needed. These procedures have been carried out quite extensively in Europe and in some tropical sugar-growing countries where from 10 to 20 per cent alcohol may be in the motor fuel, the higher amount having been employed in Sweden for many years. Similar proposals have been made for the United States and even tried in localized areas. However, the present cost of gasoline, exclusive of tax and distribution expense, is around 5 cents per gallon at the refineries and hence very much less than the cost of producing alcohol.

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[1] This corresponds to 92.423 per cent of ethyl alcohol by weight. However, when alcohol percentage strength is given, it refers to percentage by volume.

[2] 100 volumes of 100-proof alcohol contain 50 volumes of absolute alcohol and 53.73 volumes of water, owing to volume contraction.

The cost of alcohol is largely that of the raw material, as 1 gal. of 190-proof alcohol requires 2.5 gal. of molasses, or somewhat less than ½ bu. of corn.[1] It is very difficult to determine the alcohol cost, as the price of the raw material varies from place to place, as does the cost of steam and of overhead. We may, however, *approximate* this as follows for 1 gal. of 190-proof or 95 per cent alcohol:

2½ gal. molasses at 6 cents per gallon[1]	$0.150
Steam cost, 50 lb. at 20 cents per 1,000 lb	0.010
Direct labor, 0.01 man-hour at 70 cents	0.007
Water, power, repairs, miscellaneous	0.018
Factory overhead	0.007
Selling expense, insurance, taxes, general overhead	0.080
Depreciation on plant and interest on capital	0.010
Approximate cost, 190 proof per gallon	$0.282

[1] The cost of molasses has varied from 9 cents per gallon in 1937 to 6 cents per gallon in 1940. There is also usually a ½ cent per gallon differential in favor of molasses delivered at Gulf ports in comparison with North Atlantic harbors, but this is partly offset by the freight charges incurred in shipping the finished alcohol from the Gulf Coast to the industrial centers of the Middle West or of the North. This calculation can be changed as the price of molasses varies. Molasses being almost unobtainable during the Second World War, many alcohol manufacturers turned to corn or wheat for their carbohydrate.

MANUFACTURE OF INDUSTRIAL ALCOHOL

Raw Materials.—Carbohydrates are the basic materials for industrial fermentation alcohol, and delivered costs are the guiding factors as to which one is chosen. In the United States, molasses from Cuba, Puerto Rico, and the Hawaiian Islands is normally consumed very largely as Table 2 shows. Molasses is transported in tank steamer loads and then, if necessary, by barge or full trains of tank cars. Blackstrap molasses is the mother liquor from the raw sugar crystallization. In recent years a large amount of *high-test molasses* has been used[2] for fermentation and as cattle food. Occasionally low-grade grain is fermented for industrial alcohol. In wartime almost any available grain will be used—wheat and wheat flour in the United States. It should be noted that the beverage laws specify the use of grain alcohol in certain beverages (whisky), and custom demands it for some tax-paid solvent uses. Thus a demand is created for this grain alcohol, though of a competitively higher raw-material cost, using, as required by law, corn and the small grains (see Table 2).

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[1] The Federal government expects distillers to get out of 1 bu. of the moist grain, from 4.5 to 5 proof gal. of alcohol. A bushel of the moist corn as received from the farmer weighs 56 lb. and has 15 per cent moisture. Of the corn dry substance 69.5 per cent is starch and 0.5 per cent fermentable sugars, or a total of 70 per cent (33.3 lb.) starch or equivalent.

[2] Although high-test molasses has been occasionally made by dissolving, with little or no inversion, excess stocks of low-purity Cuban *raws*, the present supply comes largely from inversion and evaporation of the cane juice. This gives a *high test* with low sucrose to invert ratio of 0.4 to 0.5 as exemplified in Table 3 while the *liquid sugar* from the melting in water of raw sugar furnished a product with high sucrose to invert ratio of 10 with consequent tendency to crystallization. Note that the sucrose to invert ratio in blackstrap is roughly 2.0 to 2.5. For certain recent modifications in handling of molasses, see Reich, Molasses Elaboration, *Trans. Am. Inst. Chem. Engrs.*, **38**, 1049 (1942); Bilford, Scalf, Stark, and Kolachov, Alcoholic Fermentation of Molasses, *Ind. Eng. Chem.*, **34**, 1406 (1942).

TABLE 2.—ETHYL ALCOHOL: SUMMARY OF OPERATIONS OF PLANTS AND OF MATERIALS USED, FISCAL YEARS 1940 AND 1941[a]

	1940	1941
Number of plants operated	37	39
Number of bonded warehouses operated	65	62
Operations (proof gallons):		
Production	243,727,756	298,845,417
Removed to bonded warehouses	242,128,867	297,331,825
Withdrawals from bond, total	251,820,728	309,505,095
Tax-paid	24,344,306	27,866,523
Tax-free, total	227,476,422	281,638,572
For denaturation	223,321,704	274,887,261
For hospital and scientific use	2,033,903	2,135,668
For use of U.S. and subdivisions	1,224,504	3,696,008
For export	196,284	394,078
For medicinal, beverage, and other authorized uses in Puerto Rico	700,027	525,557
Losses in warehouses	496,294	697,140
Losses in transit	42,813	47,451
Stocks in bonded warehouses, June 30	21,798,554	10,392,352
Materials used:		
Molasses, gal	194,601,378	221,820,392
Grain:		
Corn, lb	136,815,670	171,818,129
Malt, lb	16,851,377	17,623,062
Rye, lb	4,460,927	12,037,907
Other, lb	41,893	16,452
Ethyl sulfate, gal	45,785,850	53,399,664
Sulfite liquor, gal	10,379,740	
Crude alcohols mixture, gal	3,419,737	2,365,256
Pineapple juice, gal	3,255,920	1,831,381
Cellulose pulp and chemical mixture, lb	10,124,665	15,365,950
Corn sugar by-product, hydrol, lb	1,205,271	2,245,793
Potatoes, lb	703,010	686,585
Potato residue, lb	371,823	
Diamalt, lb	21,759	15,066

[a] From U.S. Bureau of Internal Revenue, "Statistics on Alcohol," 1941. Later statistics are not available during the national emergency. However, it has been estimated that during 1944, the production of industrial alcohol is at the rate of over 600,000,000 wine gallons, of which 300,000,000 are for synthetic rubber.

In England, molasses is generally used; in France, beets and beet-sugar molasses; in Germany and Russia, potatoes are usually most economical. Cellulose from wood has been much written about as a source for the sugars to be fermented, and this raw material is employed, particularly in Germany where cheap molasses is not available. However, in the United States a recent large-scale attempt to base alcohol on wood has not proved competitive with molasses, owing largely to the cost of converting the wood to the fermentable sugars.

TABLE 3.—ANALYSIS OF BLACKSTRAP, HIGH-TEST, AND BEET MOLASSES
(The blackstrap and high-test are of Cuban cane origin)

	Blackstrap	High-test	Discard beet
Pounds per gallon	12.0 -12.1	12.10–12.12	12.30–12.37
Sucrose, per cent by weight	40.36–34.20[a]	22.73–26.83[a]	48.0 -51.5
Invert sugar, per cent by weight	16.99–19.57[a]	55.47–51.45[a]	Less than 1 per cent
Raffinose	....	....	1.6 - 4.2
Nonsugar solids, per cent by weight	28.81–35.57	7.5 - 6.8	30.4 -27.3

[a] The sum of the sucrose and the invert sugars usually amounts to 55 per cent by weight ± 2 per cent for the blackstrap, and from 70 to 80 per cent for the high-test molasses. The beet molasses has from 11 to 13 per cent ash.

Reactions.—The principal reactions in alcohol fermentation are *Equation of inversion:*[1]

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{d\text{-Glucose}}{C_6H_{12}O_6} + \underset{d\text{-Fructose}}{C_6H_{12}O_6}$$

Equations of fermentation:[2]

$$\underset{\text{Monosaccharide}}{C_6H_{12}O_6} \rightarrow \underset{\text{Alcohol}}{2C_2H_5OH} + 2CO_2; \qquad \Delta H = -31{,}200 \text{ cal.} \qquad (1)$$

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[1] In commercial parlance, reducing or invert sugars are fermented and include the scientific *d*-glucose and *d*-fructose. The product sold commercially as glucose is usually a sirup of *d*-glucose with some dextrin and maltose, while dextrose U.S.P. is *d*-glucose. For about 5 per cent of the alcohol normally produced in the United States, starch from corn (see p. 636) is hydrolyzed; in Europe much starch from potatoes is used as a source of glucose for fermentation.

[2] This is the classic Gay-Lussac equation for alcohol formation. It is the principal equation in acid or low pH medium. When growing yeast for sale as such or for inoculation, usually with some air blown in, the yield of alcohol is lower, it being partly changed to CO_2 and H_2O. However, this fermentation, like so very many industrial reactions, is very much more involved than these simple reactions indicate. Probably the first step is a phosphate hexose ester formation, followed by a split in the six-carbon chain. *Cf.* WHITMORE, "Organic Chemistry," pp. 107–108, D. Van Nostrand Company, Inc., New York, 1937; MICHAELIS, Chemistry of Alcoholic Fermentation, *Ind. Eng. Chem.*, **27**, 1037 (1935). The fusel oil (mixed amyl alcohols with some propyl, butyl, and hexyl alcohols and esters), amounting to 3 to 11 parts per 1,000 of alcohol, obtained from yeast fermentations, is held to be furnished by the

Toward the end of a fermentation, the acidity and glycerine increase. Neuberg's third equation may account for this.

$$\underset{\text{Monosaccharide}}{2C_6H_{12}O_6} + H_2O \rightarrow \underset{\text{Alcohol}}{C_2H_5OH} + \underset{\substack{\text{Acetic}\\ \text{acid}}}{CH_3COOH} + 2CO_2 + \underset{\text{Glycerine}}{2C_3H_8O_3} \quad (2)$$

There is always found in alcohol fermentations a small amount of glycerine.

Energy Requirements, Unit Operations, Unit Processes.—The shipment of raw material may involve tank-car movement of molasses to the Cuban or Puerto Rican shore, steamer to an American (or other) port, and barge or tank train[1] transhipment to a plant, if inland. The plant procedures require steam heating for distillation, power for pumping, and water for condensation and occasionally for cooling during the exothermic fermentation. The heat evolved by this fermentation reaction calculates to 88,940,000 kg.-cal., or 353,000,000 B.t.u. per 1,000 gal. of 95 per cent alcohol. Its evolution is usually spread over several days.

The manufacture of alcohol, as presented in Fig. 1, can be broken down into the following principal *unit processes* (Pr.) and *unit operations* (Op.). The main steps in the competitive manufacture of alcohol from petroleum cracking (*cf.* Esterification Chap. XXXIX) are shown in parallel comparison.

Fermentation Alcohol	*Alcohol from Ethylene*
Transportation of molasses or corn (Op.).	Liquefaction of the petroleum gases containing ethylene (Op.).
Storage of molasses or corn (Op.).	Rectification to produce pure ethylene and pure ethane (Op.).
Grinding, etc., of corn (Op.).	Dehydrogenation of ethane to ethylene (Pr.).
Hydrolysis by heating of cornmeal with malt or acid to make mash (Pr.).	Esterification of strong sulfuric acid by ethylene (Pr.).
Growth of inoculating cultures (Pr.).	Hydrolysis of diluted ester to alcohol and diluted sulfuric acid (Pr.).
Fermentation of diluted inverted molasses or of corn mash (Pr.).	Distillation of alcohol from acid (Op.).
Distillation of alcohol from "beer" (Op.).	Rectification and purification of alcohol (Op.).
Rectification and purification of alcohol (Op.).	Concentration of diluted sulfuric acid to strong acid (Op.).
Recovery of by-products, *e.g.*, CO_2, feed, potash salts (Op.).	Recovery of by-products, *e.g.*, CO_2 (Op.).

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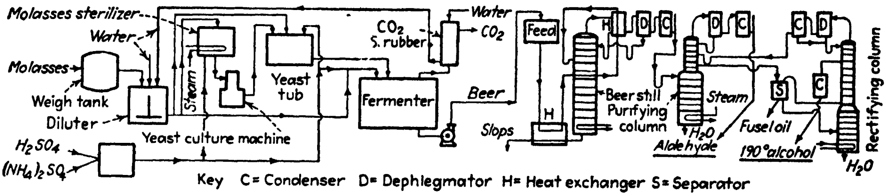
protein materials in the *mash* fermented. *Cf.* PRESCOTT and DUNN, "Industrial Microbiology," Chap. IV, McGraw-Hill Book Company, Inc., New York, 1940.

[1] Recently, the U.S. Interstate Commerce Commission has allowed the railroads to make special (low) freight charges for entire trainload shipments of tank cars of molasses.

Making of Industrial Alcohol.—The flow sheet in Fig. 1 shows the various operations and processes involved in changing molasses into salable alcohol. Molasses, because of the strong concentration of sugar (Table 3), does not support direct yeast fermentation.[1] It must be diluted first to a concentration of about 10 per cent sugars. This is called the *mash* and represents the carbohydrate ready for yeast inoculation. It is pumped to a large steel fermenter[2] (60,000 to 500,000 gal.), closed in many modern plants to collect the carbon dioxide evolved and to afford easier conditions for cleaning and sterilizing. An ammonium salt and sulfuric acid are added, the one to furnish a nutritive constituent deficient in molasses, and the other the right environmental pH to facilitate the activity of the selected yeast and to suppress the multiplication of wild yeasts or bacteria.



Molasses	2.5 gal.	Process water	10 gal.	Per gal. 190 proof alcohol
H_2SO_4 (60° Bé.)	0.17 lb.	Cooling water	42 gal	
$(NH_4)_2SO_4$	0.015 lb.	Electricity	0.11 Kw-hr	
Steam	50 lb.	Direct labor	0.01 man-hr.	

FIG. 1.—Flow sheet for industrial alcohol.

In the meanwhile a charge of the selected yeast (about 5 per cent of total volume) has been growing in the yeast tub. Very carefully controlled conditions are used to furnish only the desired strain of yeast. All of this is under exact laboratory supervision, including the selection of the inoculating yeast strain, the sterilization of the diluted molasses, the addition of the nutrients, the pH, the temperature (76°F.), and finally the cleaning and sterilizing of the yeast culture machine in readiness for the next batch. The bacteriologists have been able to cultivate a strain of yeast that thrives under these acid conditions, while wild yeast and bacteria do not. It is very seldom that beet molasses or hydrol (mother liquor from corn dextrose crystallization) is used for industrial alcohol in this country. These require special treatment. As the reaction study indicates, the fermentation is exothermic and so cooling by outside sprays is frequently used; hence one advantage of the steel fermenter. Although the most favorable temperature varies, it is usually around 70°F. for starting and under 100°F. at the end. Four days are allowed by governmental regulations for a fermentation cycle, though usually 48 to 72 hr. are used. As alcohol is formed by yeast only from monosaccharides, it is necessary to split the sucrose, $C_{12}H_{22}O_{11}$, into *d*-glucose and *d*-fructose.[1] In alcohol fermentation by yeast, this microorganism furnishes an organic catalyst, or enzyme, known as *invertase* which effects this hydrolysis. The yeast also produces another and more important enzyme, *zymase*, which changes the monosaccharides into alcohol and carbon dioxide. The flow sheet of Fig. 2, Chap. VIII outlines the procedure for purification of the carbon dioxide from fermentation. Such recovery is practiced from a number of different fermentations—industrial alcohol, whisky, and butanol-acetone.

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[1] Indeed strong sugar sirup is a *preservative;* witness the preserving of fruits with it.

[2] Wood in many of the older plants.

The liquor in the fermenters after the action is finished, is called a *beer.*[2] The alcohol is separated by *distillation.* In such fermentation as pictured in Fig. 1, the beer, containing about 6.5 to 8.5 per cent alcohol by volume, is pumped to the upper sections of the beer still, after passing several heat exchangers as shown. As the beer passes down the beer column, it gradually loses its lighter boiling constituents, namely, alcohol and a small amount of aldehydes. The liquid discharged from the bottom of the still through a heat exchanger is known as *slop* or *stillage.* It carries proteins, some residual sugars, and, in some instances, vitamin products so that frequently it has been evaporated and used as a constituent of cattle feeds. The overhead containing alcohol, some water, and the aldehydes passes through a heat exchanger to the partial condenser or dephlegmator, which condenses sufficient of the vapors to afford a reflux and also to strengthen the vapors that do pass through to the condenser where about 50 per cent alcohol, containing the volatiles or aldehydes, is condensed. This condensate, frequently known as the *high wines,* is conducted into the aldehyde or heads column, from which the low-boiling impurities, or aldehydes, are separated as an overhead. The effluent liquor from part way down the aldehyde column flows into the rectifying column.

In this third column the alcohol is brought to strength and finally purified in the following manner: The overhead going through a dephlegmator is partly condensed to keep the stronger alcohol in this column and to provide reflux for the upper plates. The more volatile products, which may still contain a trace of aldehydes and of course some alcohol, are totally condensed and carried back to the upper part of the aldehyde still. Near the top of the column 95 to 95.6 per cent alcohol is taken off through a condenser for storage and sale. Farther down the column, the higher boiling fusel oils are run off through a cooler and separator to a special still where they are separated from any alcohol they may carry, before being sold as an impure amyl alcohol for solvent purposes. The bottom of this rectifying column[1] discharges water.

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[1] An equimolecular mixture of these is known as *invert* sugar and results by the action of heat, acids, or enzymes.

[2] This is a general term applied to the result of any such fermentation, whether it results finally in industrial alcohol or the beverage beer, or whisky, or butanol and acetone.

Alcohol-water mixtures are rectified to increase the strength of the alcohol component by virtue of the composition of the vapors being stronger in the more volatile constituent than the liquid from which these vapors arise. This is shown quantitatively by the curves of Fig. 2 where the composition of the vapor in equilibrium with the liquid is on a horizontal line. However, alcohol cannot be made stronger by rectification than 95.6 per cent because, as can be seen from Fig. 2, water forms a binary constant boiling mixture of this composition which boils slightly lower than absolute or anhydrous alcohol. The principles shown here

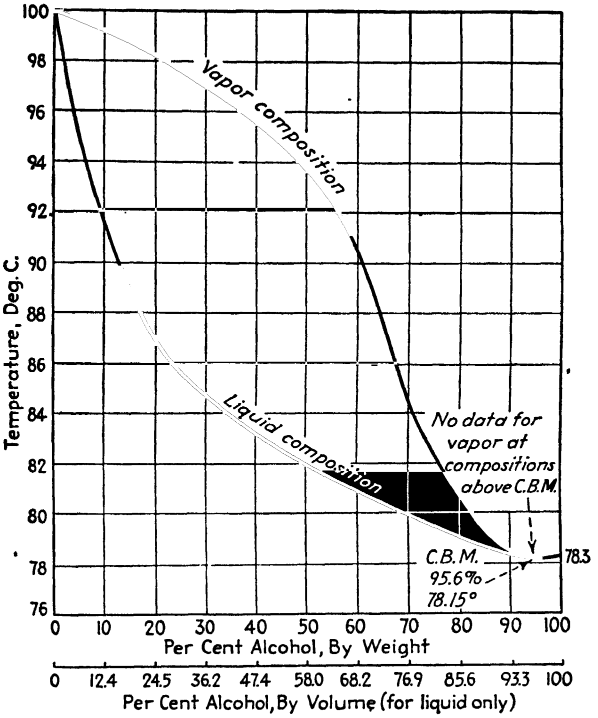

FIG. 2.—Temperature vs. composition of vapor and liquid for alcohol—water at 760 mm.

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[1] Further details with excellent pictures of a somewhat similar plant to that of Fig. 1 are given by Reich, Modern Molasses Distillery, *Chem. & Met. Eng.*, **41,** 64 (1934); Anon., Modern Molasses Distillery, *Chem. & Met. Eng.*, **46,** 365 (1939), pictured flow sheet. *Cf.* OWEN, Motor Fuel from Molasses, *Sugar*, **39,** No. 4, 26 (1944); CAREY and LEWIS, Studies in Distillation, *Ind. Eng. Chem.*, **24,** 882 (1932).

are the basis of the strengthening of the more volatile constituent of any liquid mixture by distillation.

The Second World War has greatly stimulated the production of alcohol to meet the demands of a nation at war; it has also forced a change to other raw materials such as corn and wheat because of the temporary unavailability of molasses.[1] Whisky plants have been converted to the manufacture of industrial alcohol and many changes have been made in the equipment,[2] even to the temporary use of wooden fractionating towers. To lessen contamination from the discard slop or stillage when fermenting grain, the wheat, for instance, is milled to a granular flour for fermentation and the separated bran and outer part of the wheat[3] grain are sold for cattle feed. Even waste sulfite liquors are being converted to alcohol in wartime to meet the enhanced demand at higher prices.

ABSOLUTE OR ANHYDROUS ALCOHOL[4]

Anhydrous alcohol was made by absorbing the 5 per cent of water present in 95 per cent industrial alcohol, using quicklime, with subsequent distillation. This process was expensive and, although it produced a very high quality of anhydrous alcohol, it has now been superseded largely by improved chemical engineering unit operations of distillation and extraction involving a third component. This has led to lower cost of dehydrating operations, mostly of a continuous nature using preferably all liquids or solutions, and has resulted in reducing the price of anhydrous alcohol to a figure only slightly in excess of the usual selling value of the alcohol contents. These newer procedures involve improvements both in dehydrating agents and in the continuous columns used.

According to D. B. Keyes,[5]

> . . . the basic principle of a dehydrating agent, when used in a fractionating column to produce anhydrous alcohol from wet alcohol, is the effect of the dehydrating agent on the partial pressure of the alcohol and of the water. In other words, there are two classes of dehydrating agents used in fractionating columns for this purpose. One depresses the partial pressure of the water more than the

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[1] SINGLETON, Wartime Developments in the Alcohol Industry, *Chem. Industries*, **52**, 450 (1943).

[2] REICH, Getting More Alcohol from Present Facilities, *Chem. & Met. Eng.*, **49**, No. 5, 129–131 (1942).

[3] CALLAHAM, From Waste Liquors to War Alcohol, *Chem. & Met. Eng.*, **50**, No. 12, 104 (1943).

[4] This is practically 100 per cent ethyl alcohol and is frequently known as *absolute* alcohol but, as the absence of water is more notable than that of other impurities, the term *anhydrous* alcohol is preferred by some.

[5] *Private communication. Cf.* KEYES, The Manufacture of Anhydrous Ethyl Alcohol, *Ind. Eng. Chem.*, **21**, 998–1001 (1929); OTHMER, Partial Pressure Processes, *Ind. Eng. Chem.*, **33**, 1107 (1941).

alcohol and the other depresses the partial pressure of the alcohol more than the water. In the first instance, the alcohol goes out of the top of the column, and in the second instance, out of the bottom. The dehydrating agent functions according to the above-mentioned principle. For example, lime, anhydrous calcium sulfate,[1] or any solid dehydrating agent will naturally come out of the bottom of the column and must carry the water with it, forcing the alcohol to come out of the top. Glycerine and ethylene glycol being high-boiling constituents have a tendency to be removed at the bottom of the column and are useful because they depress the partial pressure of the water more than the alcohol and, therefore, carry the water with them, permitting the alcohol to come out at the top of the column. Ether, benzene, ethyl acetate, toluene, hexane, or carbon tetrachloride,[2] on the other hand, are much more volatile constituents than the glycerine and glycol and also have a tendency to depress the partial pressure of the alcohol more than the water. Therefore, they are removed with the water at the top of the column and the anhydrous alcohol leaves at the bottom.

The water in 95 per cent alcohol is removed technically by either of two principal methods: (1) Dehydration by *distillation with a third component*[3] which forms a minimum constant boiling mixture in the system, boiling at a lower temperature than the 95 per cent alcohol (78.15°C.) or the water. Here (*a*) the minimum is a binary one, of which water-ethyl ether is an example,[4] or (*b*) the minimum is a ternary one of which alcohol-water-benzene is an example. In such instances anhydrous alcohol is obtained at the bottom of the distilling column, because its vapor pressure is relatively lower than that of the constant boiling mixture removing the water. (2) Dehydration by *countercurrent extraction*[5] usually also in a continuous column with a third component which depresses the vapor pressure of water more than it depresses the vapor pressure of alcohol, *e.g.*, glycerine, ethylene glycol, glycerine or glycol with dissolved salts, molten eutectic mixture of Na and K acetates. Anhydrous alcohol comes out the top of the extraction column.[6]

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[1] WALLIS, *Intern. Sugar J.*, **38,** 217–219 (1936). This process used a solid absorbent $CaSO_4$ changing to the hemihydrate.

[2] Other withdrawing agents employed are trichloro-ethylene or a petroleum fraction, or other liquid fairly insoluble in water and boiling in the range 30 to 120°C.

[3] This third component is frequently called a *dehydrating* or *withdrawing agent* or simply an *entrainer*.

[4] OTHMER and WENTWORTH, Absolute Alcohol, *Ind. Eng. Chem.*, **32,** 1588–1593 (1940). Here the water is removed overhead by ether, the system being under 100 lb. pressure.

[5] OTHMER and TRUEGER, Recovery of Acetone and Ethanol by Solvent Extraction, *Trans. Am. Inst. Chem. Engrs.*, **37,** 597–619 (1941).

[6] The use of a solid dehydrating agent, such as quicklime or calcium sulfate, may be looked upon as an extreme case of this method, though usually run in a discontinuous manner because of the solid involved.

The basic principle of the process using benzene as a withdrawing agent is illustrated[1] by Fig. 3. There are three binary minimum constant boiling mixtures in the system, two homogeneous ones and one heterogeneous one (between water and benzene), and a ternary minimum constant boiling mixture which is the lowest boiling composition in the system, boiling at 64.85°C.

In Fig. 3 the composition of the ternary[2] minimum constant boiling mixture is represented by point *F*. In order that the removal of the c.b.m. from the starting mixture shall leave anhydrous alcohol in the still, the starting composition must lie on the straight line *CF*. If the starting mixture is to be made up by adding benzene to 95 per cent alcohol, the starting composition must also lie on the line *EB*. Therefore, the intersection *G* represents the starting composition. If enough benzene is added to 95 per cent alcohol to bring the total composition to point *G*, continuous distillation gives the ternary constant boiling mixture (boiling point, 64.85°C.) at the top of the column and absolute alcohol (boiling point, 78.3°C.) at the bottom of the column in a simple distillation.

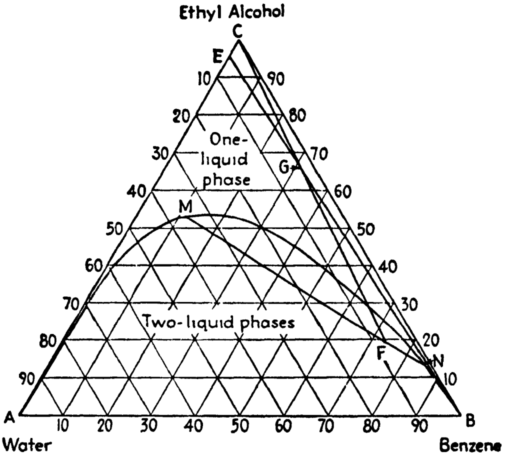

FIG. 3.—Ternary diagram of liquid system. Water-alcohol-benzene

An important[3] feature of the process is the separation of the condensate into two liquid layers, represented in Fig. 3 by points *M* and *N*. The ratio of the top layer *N* to the bottom layer *M* is equal to *MF/FN*. The compositions involved are

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[1] A somewhat similar procedure is the ether pressure system of Othmer and Wentworth, *op. cit.*

[2] See PERRY, *op. cit.*, pp. 1220–1222, for triangular phase diagrams.

[3] GUINOT and CLARK, Azeotropic Distillation in Industry, *Trans. Inst. Chem. Engrs.* (London), **16**, 189–199 (1938).

Ternary distillate
- 18.5 per cent alcohol.
- 7.4 per cent water.
- 74.1 per cent benzene.

Top layer of condensate at 20°C., representing 84 per cent by volume:
- 14.5 per cent alcohol.
- 1 per cent water.
- 84.5 per cent benzene.

Bottom layer of condensate at 20°C., representing 16 per cent by volume:
- 53 per cent alcohol.
- 36 per cent water.
- 11 per cent benzene.

Figure 4 illustrates how this process functions. The 95 per cent alcohol with the requisite amount of benzene[1] is introduced continuously into column *A* heated at the bottom by a closed steam coil. The ternary goes overhead through the condenser *B* to the separator and decanter *C*, or is partly returned as reflux. From the decanter, the top layer, rich in withdrawing agent, is returned to the main column *A* and the lower

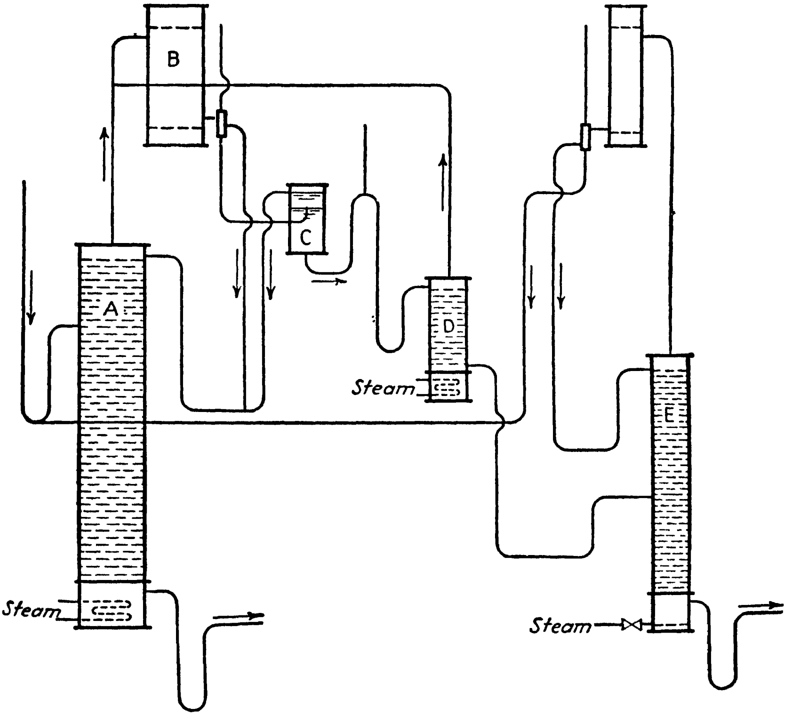

FIG. 4.—Manufacture of absolute alcohol from 95 per cent alcohol.

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[1] This withdrawing agent is used over and over again with a loss that should not exceed 0.05 per cent on the volume of the anhydrous alcohol produced.

layer, rich in water, is run to the smaller column *D*, from which the overhead as the ternary c.b.m. is passed to the main condenser *B*. From the bottom of the small column *D*, aqueous alcohol is obtained which is rectified to 95 per cent alcohol in column *E* and returned to the main column. From the base of *E* the water flows to the sewer. The product, anhydrous alcohol, passes from base of main column *A*.

These same principles of distillation in multicomponent systems, involving constant boiling mixtures, are used for dehydrating other organic liquids such as propyl alcohol and for removing the water formed in sulfonations (benzene-sulfonic acid) and esterifications (ethyl acetate).[1]

BEERS, WINES, AND LIQUORS

The making of fermented beverages was discovered by primitive man and has been practiced as an art for thousands of years. Within the past century and a half this has become a highly developed science. As Muspratt writes, "There is no department of the arts and manufactures where chemistry has exerted a more decided influence than in brewing." But E. A. Siebel adds to this, "A modern brewer has to be an engineer, a chemist, and a bacteriologist." In common with other food industries, the factors of taste, odor, yes, and of almost individual preference exist, to force the manufacturer to exert the greatest of skill and experience in producing palatable beverages of great variety. In the last analysis, the criterion of quality, with all the arts of modern science, still lies in the human sensory organs of taste, smell, and sight.

Uses and Economics.—As Table 4 indicates, many millions of barrels of alcoholic beverages are manufactured in the United States each year.

Raw Materials.—Grains and fruits supplying carbohydrates are the basic raw materials. The variety of grains and fruits employed is wide, changing from country to country or from beverage to beverage. Russia ferments potatoes and by distillation obtains vodka; similar treatment of the sap of the maguey in Mexico yields pulque; but the world's chief raw materials for fermentations are the cereals, corn, barley, and rice, together with the grape.

Making of Beer.—Beer and allied products are beverages of low alcoholic content (2 to 7 per cent) made by brewing various cereals with hops, usually added to impart a more or less bitter taste, followed by fermentation. The cereals employed are called *brewers' grains* and are barley, malted to develop the necessary enzymes and the desired flavor, as well as malt adjuncts: flaked oats, rice, and corn, with wheat used in Germany and rice and millet in China. Brewing sugars and sirups (corn sugar or glucose) and yeast complete the raw materials. For beer the most important cereal is barley, which is converted into malt by partial germination.[1]

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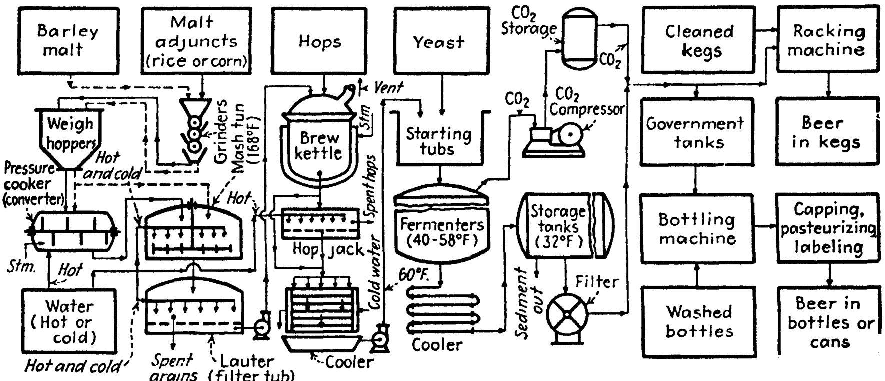
[1] GUINOT and CLARK, *op. cit.;* OTHMER, *op. cit.*

TABLE 4.—UNITED STATES PRODUCTION AND IMPORTS OF ALCOHOLIC BEVERAGES, 1939

	Production	Imports
Distilled spirits	346,344,000 gal.	10,834,000 gal.
Still wines	231,986,000 gal.	3,157,000 gal.
Sparkling wines	6,634,000 half pt.	514,000 half pt.
Rectified spirits and wines	43,401,000 bbl.	324,000 gal.
Fermented malt liquors	53,871,000 bbl.	
Cereal beverages	63,000 bbl.	

NOTE: "Gal." refers to proof gallons; "bbl." contains 31 gal. Production during the war years has been greatly dislocated by restrictions imposed on the usual raw materials.

The barley is steeped in cold water and spread out on floors, or in special compartments, and regularly turned over for from 5 to 8 days, the layers being gradually thinned as the germination proceeds. At the proper time, when the enzymes are formed, the growth is arrested by heat. During the growth, oxygen is absorbed, carbon dioxide given off, and the enzyme, diastase, formed. This latter is the biological catalyst that changes the dissolved starch into the disaccharide, maltose, which, after transformation into the monosaccharide, glucose, by the maltose enzyme, is directly fermentable by yeast.



Brewer's malt	35-38 lb.	Brewery labor	$0 50-$1 50	Per U.S. barrel (31gal.) of beer
Malt adjuncts	12-14 lb.	Power and steam	0.50-0.70	
Hops	½-1¼ lb.	Bottling costs (labor labels, alkali, etc.)	1.50-2.50	
Yeast	¾-1 lb.			

FIG. 5.—Flow sheet for manufacture of beer.

The flow sheet for beer on Fig. 5 may be divided into three groups of procedures: (1) brewing of the mash through to the cooled hopped wort,

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[1] See ANON., Brewing of Lager Beer, *Chem. & Met. Eng.*, **49**, No. 7, 112 (1942) for pictured flow sheet.

(2) fermentation, and (3) storage, finishing, and packaging for market. *Mashing* is the extraction of the valuable constituents of malt, malt adjuncts, and sugars by macerating the ground materials with water treated to prevent too high pH, which would tend to make a dark beer. In America, 35 to 38 lb. of barley malt and 12 to 14 lb. of malt adjuncts or unmalted cereals (rice, corn, or carbohydrate) are used per U.S. barrel of 31 gal. These are flaked or ground on rolls. All the unmalted cereal is mixed in the ratio of 3 parts to 1 part of ground malt. This mixture is added to water in the proportion of 1,000 lb. per 7.5 to 9 bbl. of water. The materials so treated, the converter mash, are heated in the pressure cooker in order to convert insoluble starch into soluble starch, and the soluble malt starch into dextrin and malt sugars. The resulting boiling cooker mash, mixed with the rest of the malt in the mash tube, raising the temperature to 168°F., is used to prepare the brewers' *wort.*[1] This is carried out in the mash tun. After all the required ingredients have been dissolved from the brewing materials, the entire mash is run from the mash tun to the lauter or straining tub, where the wort is separated from the insoluble spent grains through a slotted false bottom and run into the copper wort cooker. For complete recovery of all substances in solution, a spray of decarbonated water at 165°F. is rained through the grains. This is called *sparging.*

The wort is cooked for approximately 3 hr., during two of which it is in contact with hops. The purpose of boiling is to concentrate the wort to the desired strength, to sterilize it (15 min.) and destroy all the enzymes, to coagulate certain proteins by heat (180°F.), to modify the malty smell of the wort, and to extract the tannin and aroma from the hops which are added during the cooking process. At the end of the 3 hr., the spent hops are separated from the boiling wort very quickly through a false bottom in the hop jack or strainer underneath the copper cooker. Since the spent hops retain 3 bbl. of wort per 100 lb. of hops, they should also be sparged. The wort is then ready to be cooled.

The cooling step is not only to reduce the temperature but also to allow the wort to absorb enough air to facilitate the start of the fermentation. In addition, the protein and hop resins are precipitated. The hot wort may be first cooled to about 150 to 160°F. in a large shallow cooler where certain of the resins precipitate. The wort is then run over the horizontal, brine-cooled copper tubes of the open Baudelot cooler, where aeration also takes place. Slight concentration, due to evaporation, occurs. This operation is performed under controlled conditions to prevent contamination by *wild* yeasts. Frequently, sterilized air is used.

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[1] The wort is the liquid resulting from the mashing process, *i.e.*, the extracting and solubilizing of the malt and malt adjuncts. Wort composition varies from 17 to 24 per cent solids by weight for the first wort, to approximately 1 per cent solids for the last wort removed by the sparge water.

The cooled wort is mixed with selected yeasts in the line leading to the starting tubs, between ¾ and 1 lb. of yeast being used per barrel of beer. The initial *fermentation* temperature is 40 to 43°F. but, as the fermentation proceeds, the temperature rises to 58°F. This is easily explained by the fact that the conversion of the sugar to CO_2 and ethyl alcohol, by the enzymes of the yeast, generates 280 B.t.u. per lb. of maltose converted.[1] The temperature is partly controlled by attemperators inserted in the fermenters. The mixture is skimmed to remove the foreign substances that the evolved carbon dioxide brings to the top. Thus it is quite evident that a steady evolution of gas is necessary to cleanse the beer properly. The CO_2 evolved is often collected by using closed fermenters and stored under 250 lb. pressure for subsequent use in carbonating beer.

The yeast gradually settles to the bottom of the tub, so that at the end of 7 to 10 days the fermented beer is ready to be vatted. The liquid is very opalescent in appearance, under a cover of foam. As the beer leaves the fermenting cellar, it contains in suspension hop resins, insoluble nitrogenous substances, and a fair amount of yeast.

The beer is cooled to 32°F. and stored in the cellar for 3 to 6 weeks at this temperature. During this period, clarification, separation, and precipitation of hard resins and improvement in palatability (mellowing) occur. At the end of the period the beer is carbonated[2] and pumped through a pulp filter with or without such nontaste-imparting filter aids as asbestos fiber. In the United States, public demand favors a brilliant beverage.[3] As a result, the beer is sometimes refiltered through cotton pulp, keeping carbon dioxide on the entire system. About 97 bbl. of beer are produced per 100 bbl. of wort in the starting tubs. After bottling, the beer is pasteurized at 140°F.

Making of Wine.—Wine has been made for several thousand years by fermentation of the juice of the grape. Like other fermentations, many of the primitive procedures have been supplanted by improved science and engineering, to reduce costs and to make more uniform products. But now, as always, the quality of the product is largely related to grape, soil, and sun, resulting in variation in flavor, bouquet, and aroma. The color depends largely upon the nature of the grapes and whether the skins are pressed out before fermentation.

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[1] ROSENBUSCH, Brewing—The Present Situation, *Refrig. Eng.*, **26**, 251–253 (1933).

[2] The carbon dioxide should be kept free from air which would interfere with the stability and quality of the beer. The gas is pumped in close to 32°F. and amounts to between 0.36 and 0.45 per cent of the weight of the beer.

[3] Max and Leo Wallerstein have invented a process for the production of haze-free, chillproof beers by adding selective proteolytic enzymes to beer right after fermentation to split the proteins and thus delay or prevent the formation of the protein-tannin haze.

Wines are classified as natural (alcohol 7 to 14 per cent), fortified (alcohol 14 to 30 per cent), sweet or dry, still or sparkling. The fortified wines have alcohol or brandy added. In the sweet wines, some of the sugar remains.

For the manufacture of dry red wine, red or black grapes are necessary. The grapes are run through a crusher which macerates them but does not crush the seeds, and also removes part of the stems. The resulting pulp, or *must*, is pumped into 3,000- to 10,000-gal. tanks,[1] where sulfurous acid is added to check the growth of wild yeast. An active culture of selected and cultivated yeast equal to 3 to 5 per cent of the volume of juice is added. During fermentation, the temperature rises, so that cooling coils are necessary to maintain a temperature of 85°F. The CO_2 evolved carries the stems and seeds to the top, which is partly prevented by a grating floated in the vat. This allows an extraction of the color and the tannin from the skins and seeds. When the fermentation slows up, the juice is pumped out of the bottom of the vat, back over the top. The wine is finally run into closed tanks in the storage cellar where, during a period of 2 or 3 weeks, the yeast ferments the remainder of the sugar. The wine is given a cellar treatment to clear it, improve the taste, and decrease the time of aging. During this treatment the wine is first allowed to remain quiet for 6 weeks to remove part of the matter in suspension, then racked for clarification.[2] Bentonite, or other diatomaceous earth, may be used for clearing, 2 to 16 lb. being stirred into every 1,000 gal. of wine. An insoluble precipitate with the tannin is also formed. Extra tannin may also be added, the wine racked, filtered through diatomaceous earth, asbestos, or paper pulp. The wine is corrected to commercial standards by blending it with other wines and by the addition of sugar, acids, or tannins. It is standard procedure to chill some wines for removal of argols or crude potassium acid tartrate which is recovered and constitutes the commercial source of tartaric acid and its compounds. This treatment also gives a more stable finished wine. By quick aging methods it is possible to put out a good sweet wine in 4 months. These methods include pasteurization, refrigeration, sunlight, ultraviolet light, ozone, agitation, and aeration. The wine may be held at about freezing for 3 weeks to a month, and a small amount of oxygen gas bubbled in. Then the wine is racked, clarified, and further filtered in the usual manner.

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[1] In some of the modern American wineries these tanks are even larger and are constructed of concrete.

[2] During this and following periods the new wine undergoes a complicated series of reactions, resulting in the removal of undesired constituents and the development of the aroma. bouquet, and taste. Oxidation takes place, as well as precipitation of proteins and argols, and esterification of the acids by alcohols.

Distilled Liquors.—Various fermented products, upon distillation and aging, yield the distilled liquors. Figure 6 shows the flow sheet for whisky and gin. Brandy is distilled from wine or from the *marc*, which is the pulp left by racking or straining. By making a beer[1] from a grain mixture containing at least 51 per cent of corn and distilling and aging it, bourbon whisky is yielded. Similarly rye whisky must have started with 51 per cent of rye in the grain to be mashed and fermented. By inspecting the flow sheet on Fig. 6 in the light of Figs. 1 and 5, and the description accompanying them, the procedures of Fig. 6 for distilled liquors will be clear. The equipment,[2] up to the stills, in modern liquor plants is of steel, with the stills of copper. By law, the aging of bourbon or rye whisky of claimed age must take place in charred new white-oak barrels of approximately 50 gal. These are kept in bonded warehouses at 65 to 85°F. and at a preferred humidity of 65 to 70 per cent for 1 to 5 years usually. During this time an evaporation of the contents takes place, largely through the ends of the barrel staves. By reason of a more rapid

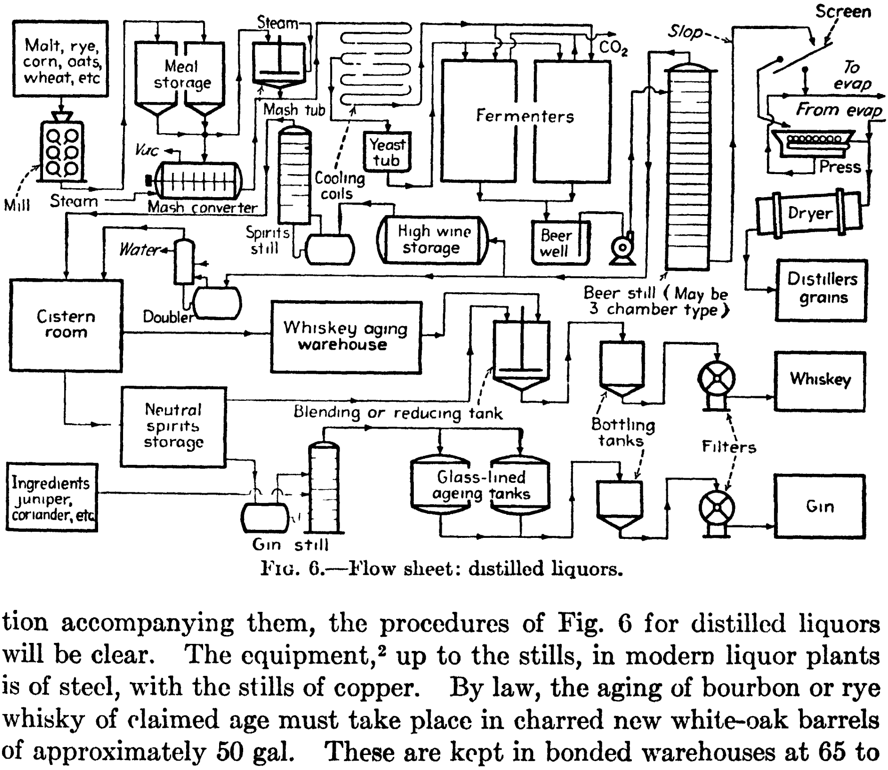

FIG. 6.—Flow sheet: distilled liquors.

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[1] The yeast in this fermentation is grown in the presence of lactic acid to ensure proper strain and to secure the desired quality of the product (whisky).

[2] OWEN, Modern Distillery Design, *Sugar*, **37**, No. 3, 26–30 (1942). In *Chem. & Met. Eng.*, **49**, No. 11, 126 (1942) is a pictured flow sheet of a grain distillery; STALLINGS and WILLKIE, Chemical Engineering Developments in a Grain Distillery, *Am. Inst. Chem. Engrs.*, **38**, 791 (1942).

capillary travel and osmosis of the smaller water molecules in comparison to alcohol molecules, an increase in percentage of alcohol is found in the barrel contents. The government shrinkage allowance is approximately 8 per cent the first year, 4 per cent the second year, 4 per cent the third year, and 3 per cent the fourth year. If the shrinkages are exceeded (and this is often the case), the manufacturer must pay a tax on the excess but, with the best cooperages under the best conditions, these allowances can just be met. The distillate from the spirit still is under 160 proof and is subsequently diluted upon barreling to 100 to 110 proof. It is *not* pure alcohol but contains small amounts of many different constituents, generally classed together as *congenerics,* which by their reaction with each other or the alcohol, or by their absorption, all catalyzed by the char of the wood, help greatly in imparting the whisky flavor and bouquet.[1] The aging whisky also extracts color and other products from the charred white oak. Changes of a like nature occur similarly on aging brandy and rum. Here, as in other divisions of the fermentation industries, skill and scientific knowledge aid in the production of a palatable product. By law, whisky must be fermented from whole grains, so that the germs (containing the corn oil) and the husks are in suspension in the liquor from the beer still in whisky manufacture. This discharge liquor is known as *slop* or *stillage.* As shown in Fig. 6, this is treated to recover the values by separating the solids from the liquid slop. After vacuum evaporation of the liquid[2] portion, it is added to the solids, and the mixture dried in rotating steam-heated driers to produce *distillers' grains,*[3] a valuable cattle feed.

BUTYL ALCOHOL AND ACETONE

Uses and Economics.—*n*-Butyl alcohol (butanol) and acetone from fermentation have had an interesting history, first being produced technically to supply acetone for the manufacture of smokeless powder, then operated mainly to furnish butyl alcohol, butyl acetate, and other esters for the lacquer industry. This better sale of first one product and then another is characteristic of industries in the chemical field, where more than one substance results from a process and reflects the changing demand that accompanies a growing and dynamic industry. This is further exemplified by wood and coal-tar distillations and the carrying on of many reactions in the synthetic organic field, resulting in different isomers, some of which have temporarily filled the warehouses. Such unbalanced markets call for much effort on the part of sales and management and have been the incentive for extensive research to vary production or to find new markets for the less easily sold products.

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[1] LIEBMANN and ROSENBLATT, Changes in Whisky While Maturing, *Ind. Eng. Chem.*, **35**, 995 (1943).

[2] This liquid contains vitamins according to Boruff, Langlykke, and Black, *Ind. Eng. Chem.*, **32**, 1239 (1940).

[3] COOLEY, Distilling By-products, *Ind. Eng. Chem.*, **30**, 615–621 (1938).

The production of normal butyl alcohol and of acetone amounted to somewhat over 100,000,000 and 200,000,000 lb., respectively, during 1940. The trend in the consumption of these solvents is upward. However, other processes contribute to the making of these products,[1] particularly butyl alcohol by hydrogenation of crotonaldehyde, and acetone by dehydrogenation of isopropyl alcohol.

Raw Materials.—The bacterial fermentation giving acetone and butanol was developed by Chaim Weizmann[2] in England and is known familiarly as the *B. Y. fermentation.* The microorganism that he used worked on starch; consequently it was a logical step, particularly during the First World War, to start this procedure on a large scale in America where corn was readily available. The Commercial Solvents Corporation was organized for this bacterial manufacture of acetone and butanol. They built plants in the corn belt both at Terre Haute, Ind., and later at Peoria, Ill., to carry on these operations. The Peoria plant is the largest of its type in the world and has many 50,000-gal. fermenters. Weizmann and his successors, when fermenting corn, used bacteria of the type *Clostridium acetobutylicum.* With the advent of manufacture of butyl alcohol and of acetone by processes other than fermentation, competition forced the abandonment of corn in favor of the lower priced by-product molasses as raw material for fermentation. The sugar in solution as molasses is transported by tank steamers from Cuba to New Orleans and by barges up the Mississippi and Illinois rivers or by full trains of tank cars to Peoria. The Weizmann starch-fermenting bacteria do not work so well commercially on sugar mashes. A number of special sugar-fermenting butyl alcohol and acetone-producing bacteria have been isolated and cultivated.[3] These sugar-fermenting bacteria, among which are *Clostridium saccharo-butylacetonicum liquefaciens,* if inoculated on sugar without any pH control, produce increasing quantities of acetic and butyric acids which very materially reduce the production of solvents. However, in the right environment and pH, with the proper nutrients, good yields of these solvents are obtainable from the fermentation of molasses.

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[1] Chapter XXXIX.

[2] Brit. Pat. 4845 (1915); U.S. Pat., 1315585. Weizmann used much of his large royalties from this process to help finance his interest in the Zionist movement of which he became the head in 1920. See particularly Chap. XII in Prescott and Dunn, *op. cit.*

[3] Mueller, U.S. Pat., 2132039 (1938); Woodruff, *et. al.,* U.S. Pat., 2089522 (1938); Arzberger, U.S. Pat., 2139108 (1938).

In order to keep down the acid,[1] alkaline compounds are employed, thus maintaining the final hydrogen-ion concentration at the optimum pH for these bacteria to give the highest yields of the neutral solvents. This fermentation process is thus being enabled to use either corn or molasses as the raw material.

Reactions.—The action of the bacteria on starch has been very carefully studied[2] and Fig. 7 gives the best hypothesis as to the course of this fermentation.

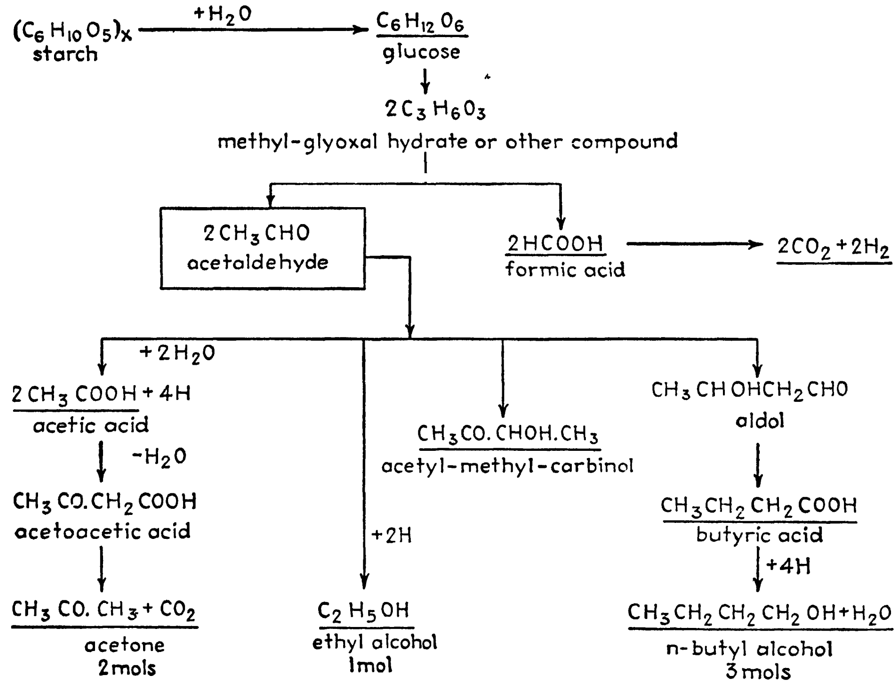

FIG. 7.—Degradation of carbohydrates by *Cl. acetobutylicum*. Known products are underlined. (*After Peterson and Fred.*)

Manufacturing Procedure.—The flow sheet on Fig. 8 illustrates the fermentation[3] of either starch or sugar, furnishing butanol, acetone, and other products. Most of the apparatus outlined in this flow sheet is made of steel except the stills which are constructed of copper. The process, when starting from corn, goes through the usual operation of separating the corn oil, the germ meal, and the husks from the starch, which is made into mash by mixing with hot water and cooking. The steam cooking not only disperses the starch into a so-called *soluble* form available for the bacteria to act on but at the same time sterilizes it so that the unwanted microorganisms are killed. At one time, the Terre Haute factory became contaminated with other bacteria[1] which grew and multiplied even more rapidly than the Weizmann bacteria, which divided and doubled in 20 min. Thus the available food was consumed by the invaders, and the yield of solvents greatly decreased. Now, complete sterilization following each batch fermentation, coupled with exact selection and cultivation of only the selected microorganisms, ensures the desired fermentation.

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[1] MUELLER, *op. cit.*

[2] PETERSON and FRED, Butyl-Acetone Fermentation of Corn Meal, *Ind. Eng. Chem.*, **24**, 237 (1932).

[3] GABRIEL, Butanol Fermentation Process, *Ind. Eng. Chem.*, **20**, 1063 (1928); GABRIEL and CRAWFORD, Development of the Butyl-Acetone Fermentation Industry, *Ind. Eng. Chem.*, **22**, 1163–1165 (1930); ARROYO, Utilization of Waste Molasses in the Production of Acetone, Butanol, and Butyric Acid., *J. Agr. Univ. Puerto Rico*, **18**, 463–479 (1934).

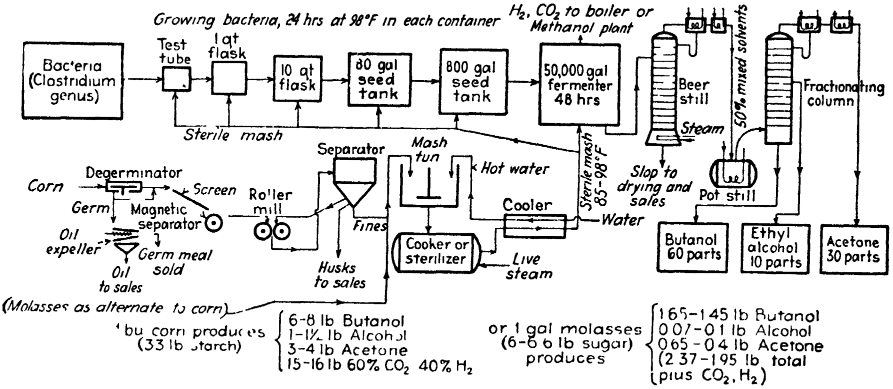

FIG. 8. - Flow sheet: butanol and acetone by fermentation.

The respective desired bacteria are carefully cultured in the laboratory by skilled and experienced bacteriologists who, after they have satisfied themselves that they have secured a pure culture, inoculate the sterile mash in increasing quantities from a test tube up to the 800-gal. seed tank, as shown in Fig. 8. In the meanwhile the main mash has been prepared and pumped into the 50,000-gal. fermenter through a heat exchanger, lowering the temperature to 98°F. for the starch mash, and to about 85°F. for the molasses mash.[2] The fermentation proceeds with the liberation of the hydrogen and carbon dioxide (60 per cent CO_2 and 40 per cent H_2), which are used for the manufacture of methanol or burned for fuel.

After 36 to 48 hr. the fermentation is ended and the *beer*, containing around 1.5 to 2.5 per cent solvents, is pumped to the beer still. The yield of the neutral solvents is 30 per cent and up, on the weight of the starch from corn or (30 per cent and up on the weight) of the fermentable sugar in molasses. In addition there is evolved about 1.5 times the weight of solvents in gases (60 per cent CO_2 and 40 per cent H_2 by volume).

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[1] KELLY, "One Thing Leads to Another," p. 32, Houghton Mifflin Company, Boston, 1930.

[2] MUELLER, *op. cit.*

The beer still consists of a continuous column containing plates, one on top of the other, yielding as vapor overhead, 50 per cent mixed solvents. The discharge from the beer still is known as *distillers' slop* or *stillage* and, as is true of a number of these fermentation operations, is a solution containing a very considerable quantity of proteins, fats, and carbohydrates, of value in animal feeds.

Recently it has been discovered[1] that the butyl alcohol-producing bacteria in their life cycle synthesize vitamins. The vitamins thus produced are riboflavin (vitamin G) and other factors of the original B complex. A concentrated riboflavin product called *Solvamin* and a riboflavin-containing feed ingredient are now being manufactured by the butyl fermentation process.

The 50 per cent mixed solvents obtained from the beer still are rectified through careful fractionation, yielding pure butanol, 95 per cent ethyl alcohol, and pure acetone. This butanol is the normal butyl alcohol. This fractionation furnishes initially fractions rich in acetone, alcohol, and butanol. Careful rectification yields the pure products. The fraction rich in butanol[2] is a mixture of 85 per cent butanol and 15 per cent water (by volume) boiling at 92.25°C. at 760 mm. of Hg. This is introduced into a column still where the take-off is first an azeotrope, containing 37.3 per cent of water by weight. This is condensed, whereupon it separates into two layers: an upper one with some water and a lower one with 4 per cent butanol and 96 per cent water. (This lower layer so rich in water is returned to the beer still.) The upper layer is run back to the column still. The net result is a constant withdrawing of water with an enhancement of the butanol percentage up to any desired figure.

VINEGAR AND ACETIC ACID

The aerobic bacterial (*Acetobacter aceti* or *Bacterium aceti*) oxidation of alcohol to dilute acetic[3] acid (8 per cent) is another ancient procedure, furnishing vinegar, a flavored acetic acid solution, fermented from wine, cider, malt, or dilute alcohol. If a pure dilute alcohol is fermented, pure dilute acetic acid results. The yield is from 80 to 90 per cent of theory. Air[4] must be supplied as these formulations indicate:

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[1] MINER, U.S. Pat., 2202161 (1940).

[2] *Cf.* STEVENS, U.S. Pat., 1394232 (1921).

[3] For a description of the largest factory engaged in this process, *cf.* Herrick and May, *Chem. & Met. Eng.*, **42**, 142–143 (1935).

[4] Too much air will cause losses due to further and undesired oxidation.

$$2C_2H_5OH + O_2 \rightarrow 2CH_3CHO + 2H_2O$$
$$2CH_3CHO + O_2 \rightarrow 2CH_3COOH$$

As these reactions are exothermic, either the alcohol can be slowly trickled through the apparatus, letting the heat dissipate, or it can be recirculated with special cooling.

If cider, malt, or wine is fermented, the acetic acid content of the resulting vinegar rarely exceeds 5 per cent, owing to limitations of the sugar content; if dilute alcohol is the raw material, the acetic acid may rise to 12 or 14 per cent, at which acidity the bacteria cease to thrive. If a fruit juice is turned to vinegar, certain esters are formed varying with the raw material, thus imparting a characteristic flavor.

The ancient process consisted in letting alcoholic products like wine or cider stand around in contact with air until the wine or cider *turned to vinegar.* This was a slow procedure, taking many months. The modern *quick* vinegar process, as commercially carried out, trickles the diluted alcohol, usually mixed with vinegar, down tall wooden tanks (10 ft. high by 4 ft. in diameter) packed with beechwood shavings or coke on which the bacteria find lodgment commonly as *mother of vinegar.* The acetic bacteria secrete an enzyme which causes the reaction. Air rises up through the tank.[1] This takes a week or so, but the production amounts to 5 to 8 gal. of 9 to 10 per cent spirit vinegar per 24 hr. from a 100 cu. ft. generator. Acid mashes are favorable to the acetic fermentation and oxidize rapidly; so it is customary to charge the generators with a mixture of vinegar and the alcoholic raw material. When 10 per cent (acetic acid) spirit vinegars are wanted, a mix of 8.2 per cent acetic and 2 to 2.6 per cent by volume of alcohol is charged.[2] This is made by mixing finished vinegar with dilute alcohol or low wines. If a cider vinegar is desired of 5 to 5.5 per cent acetic content, there is fed a mix containing 3.4 to 3.75 per cent acid and 2 to 2.6 per cent alcohol by volume.

Modern chemical engineering has improved the *quick process* by designing apparatus using pumps to circulate rapidly the mash over the packing, and with cooling in the recirculation to control the temperature low enough for favorable action of the acetic bacteria, or with special devices to ensure an adequate air supply.[3] Such designs permit the use of large generators, even up to 10,000 gal. capacity. In line with studies on other fermentations, it has been found that the acetic bacteria also need, for best conversion of alcohol to acetic acid, the proper minor foods or *nutrients* that contain sugars and the necessary inorganic salts, such as phosphates.

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[1] By keeping cider or wine casks full, so that no air is present, the vinegar formation cannot take place. Likewise, the fortified wines (above 15 per cent) have so much alcohol present that the *A. aceti* cannot function, so these wines *stay sweet.*

[2] HASSACK, Vinegar Manufacture in the United States, *Chem. Age,* **29,** 105 (1921).

[3] FRINGS, Manufacture of Vinegar, U.S. Pat., 1880381 (1932); OWENS, Vinegar Generator, U.S. Pat., 2089412 (1937); HANSEN, Making Vinegar by the Frings Process, *Food Industries,* **7,** 277 (1935).

Commercially, dilute acetic acid (8 to 10 per cent) is made this way. The process is economical if the dilute acetic can be utilized. Backhaus[1] patented a process to make ethyl acetate using dilute acetic acid, wherein the ethyl acetate is removed from the reaction by a constant boiling mixture of ethyl acetate 83 per cent, alcohol 9 per cent, and water 8 per cent. At the same time, the removal of the ethyl acetate forces the esterification equilibrium to a more favorable yield of the ethyl acetate. Acetic acid is also manufactured on a large scale (*cf.* Chap. XXXIX) through the controlled oxidation of acetaldehyde, which is made either by hydration of acetylene or by vapor phase oxidation of alcohol.

CITRIC ACID

Citric acid is one of our very widely employed acids, its production in the United States amounting to over 13,000,000 lb. for 1939. Some of this production, however, was exported. Considerably over one-half of the domestic consumption is in the medicinal field, including the manufacture of citrates and effervescent salts. About 15 per cent enters into the making of foods, 9 per cent in candy and soft drinks, and smaller amounts in the silvering of mirrors, as an ink ingredient in engraving, dyeing, and calico printing.

This acid occurs in nature in the juice of lemons, limes, oranges, and grapefruit. It is extracted from citrus juices made from off-size or off-grade fruit, by clarification, precipitation as calcium salt, with freeing of the citric acid by dilute sulfuric, followed by concentration and crystallization.

Until a short time ago the market was supplied by this natural product, but now, owing to the classical researches by Currie,[2] about two-thirds of our production of citric acid is understood to be manufactured by fermentation of sucrose by a strain of *Aspergillus niger*. Indeed this process influences the world's trade, and its product competes in foreign markets. Although no information has been published, it appears that this process is an aerobic one, the mold flourishing as a surface mycelium on the sugar solution, held in shallow pure-aluminum trays (approximately 43 by 43 by 2 in.) for probably less than 9 days. The microorganism effects an oxidation corresponding to the reaction:[1]

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[1] Backhaus, U.S. Pat., 1425625, Aug. 14, 1922; *Cf.* Keyes, Esterification Processes and Equipment, *Ind. Eng. Chem.*, **24**, 1097 (1932), Groggins, "Unit Processes in Organic Synthesis," 2d ed., p. 572, McGraw-Hill Book Company, Inc., New York, 1938.

[2] Currie, The Citric Acid Fermentation of *Aspergillus niger*, *J. Biol. Chem.*, **31**, 15 (1917); May and Herrick, Production of Organic Acids from Carbohydrates by Fermentation, *U.S. Dept. Agr. Circ.* 216 (1932); Wells and Herrick, Citric Acid Industry, *Ind. Eng. Chem.*, **30**, 255–262 (1938); Doelger and Prescott, Citric Acid Fermentation, *Ind. Eng. Chem.*, **26**, 1142 (1934).

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O + 3O_2 \rightarrow 2\underset{\substack{\text{Citric}\\\text{acid}}}{C_6H_8O_7} + 4H_2O$$

Whereas some of the sugar is utilized by the organism's respiratory activity, being converted to CO_2 and other products, yet the yields are good.

Currie showed that the formation of oxalic acid could be suppressed and good yields of citric obtained from the sucrose by starting fermentation in an acid medium at pH 3.5, at probably 30°C., and supplying suitable nutrient nitrogen by low concentrations of ammonium nitrate. Using sugar concentrations of 15 to 20 per cent, high yields, amounting to 60 per cent by weight of the sugar taken, are obtained.

It can well be imagined how expensive it is to sterilize, fill, handle, and empty the thousands of such trays needed to make the large-scale production now available. So it is no wonder that mycologists like Herrick and May[2] have studied deep air-agitated fermentation. A pilot plant has been operated on such equipment by the Bureau of Chemistry and Soils, working to produce gluconic acid. Perhaps such improvements can be applied to citric acid.

This fermentation citric acid process is one of our outstanding recent technical accomplishments. How a straight carbon-chain compound like sugar is transformed to a branch chain has so far not brought forth any plausible explanation. Here is a case where the microorganisms are wiser than the mycologists.

LACTIC ACID

$CH_3 \cdot CH \cdot (OH)\ COOH \cdot$

Lactic acid, 2-hydroxypropionic acid, is the cause of the acid taste of sour milk, having been formed by the fermentation of milk sugar (lactose) by *Streptococcus lactis*. It is one of the earliest known organic acids. Commercially, lactic acid is manufactured by the controlled fermentation of the sugar in molasses, glucose from corn, or lactose in milk whey. More than 6½ billion pounds of whey are available each year in the United States as a by-product in the manufacture of cheese from whole milk and of casein from skim milk. However, most of this whey is employed inefficiently or wasted.

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[1] For a more detailed presentation of this reaction and other features of citric acid made by fermentation, see Prescott and Dunn, *op. cit.*, p. 36.

[2] Herrick, Hellbach, and May, Apparatus for the Application of Submerged Mold Fermentations under Pressure, *Ind. Eng. Chem.*, **27**, 681–683 (1935).

The uses of lactic acid are important for deliming in tanning[1] and for acid dyeing of wool, where more than 80 per cent of the 5,000,000 lb. (100 per cent) produced are consumed. Some lactic acid is used directly in plastics, but more is esterified[2] to furnish lacquer solvents, or plasticizers (ethyl and butyl lactate, etc.). Some enters the medical field in the form of a very pure calcium lactate for calcium metabolism derangements. Increasing amounts are used in food and beverage products because of its pleasing taste and marked preservative action. Such examples are pickles, soft drinks, and candies.

The general course of the fermentation reactions[3] may be expressed as

$$\underset{\substack{\text{Sucrose or}\\ \text{lactose}}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\substack{\text{Fructose or}\\ \text{galactose}}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \rightarrow 2CH_3CHOHCOOH$$

The commercial acid is the inactive or racemic form, consisting of a mixture of the dextro and levo forms and is sold as a solution containing about 22 or 44 or 85 per cent acid and some organic impurities.

In carrying out this reaction in industry the main raw materials used are carbohydrates such as corn sugar, molasses, or the lactose in whey. There are various lactic fermentation bacteria but probably *Lactobacillus delbrücki* is more generally used than any other type. However, this will not ferment the lactose or milk sugar where *L. bulgaricus* is necessary. If these fermentations are carried out hot, *i.e.*, at around 110°F. and at a reaction more acid than pH 5.8, contaminating organisms are discouraged. After about 12 hr. the pH reaches 5.0 when milk of lime is added from time to time, as the lactic acid fermentation progresses best with a pH between 5.0 and 5.8. After 5 or 6 days the fermentation has gone as far as it will. As the flow sheet[4] of Fig. 9 indicates, the resulting calcium lactate solution is heated for the coagulation of impurities and concentrated *in vacuo* to furnish calcium lactate solution. This may be acidified to give, as a rule, 22 per cent lactic acid solution. The commercial lactic acid solutions are dark colored and contain certain organic impurities from the original sugars. Various means have been suggested for their purification,[5] such as extraction of the lactic acid through isopropyl ether[1] to water, or by the esterification with methanol and hydrolysis to lactic acid again.

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[1] Crude lactic acid is suitable for this use.

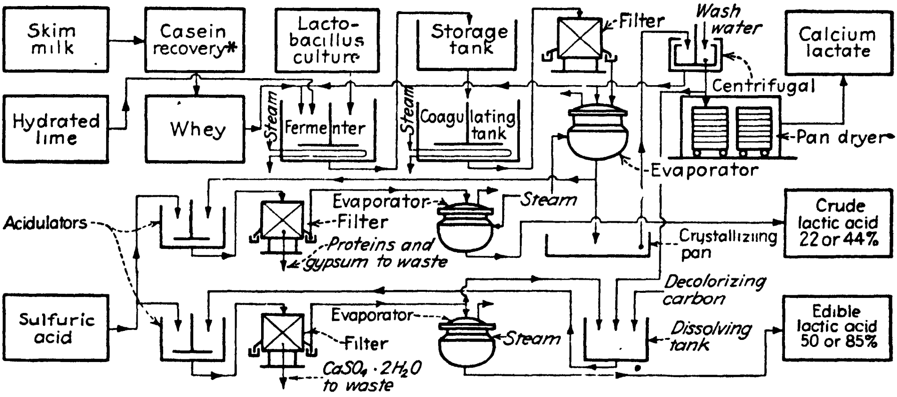
[2] SMITH and CLABORN, Lactic Esters, *Ind. Eng. Chem.*, **32**, 692 (1940).

[3] WHITTIER and ROGERS, Continuous Fermentation in the Production of Lactic Acid, *Ind. Eng. Chem.*, **23**, 532 (1931).

[4] OLIVE, Lactic Acid Manufacture from Waste Lactose, *Chem. & Met. Eng.*, **43**, 480–483 (1936); Lactic Acid and Casein from Skim Milk, *Chem. & Met. Eng.*, **47**, 427 (1940), pictured flow sheet; BURTON, By-products of Milk, *Food Industries*, **9**, 634 (1937).

[5] SMITH and CLABORN, The Production of Pure Lactic Acid, *Ind. Eng. Chem., News Ed.*, **17**, 641 (1939).

The flow sheet on Fig. 9 depicts the manufacture of edible and other purified grades by making first a calcium lactate of requisite purity by crystallization. The calcium lactate is dissolved and acidulated with sulfuric acid as shown, furnishing a 22 to 25 per cent solution of the purified lactic acid. This, or the crude acid, can be concentrated up to 50 per cent by the "building-up" process,[2] as illustrated under the respective acids in the flow sheet. This building-up process involves dissolving calcium lactate in a 25 per cent lactic acid, for example, and precipitating out the calcium by means of sulfuric acid. Calcium sulfate is removed by filtration. Lactic acid up to a 50 per cent concentration can be obtained by this method; for stronger acids a vacuum concentration in stainless-steel evaporators is necessary.



* For casein flow sheets see Fig. 7, Chap. 39 and Chem. & Met. p. 644, 1934

Whey	2,500 lb.	H_2SO_4 (100%)	58 lb.	To produce 100 lb. lactic acid, 80% yield*
$Ca(OH)_2$	100 lb.	Direct labor	Less than 3 man-hr.	

*Note: Omitting acidification, 125 lb of calcium lactate would be produced.

FIG. 9.—Flow sheet: lactic acid from whey.

PENICILLIN

The product of the activity of *Penicillium notatum* is penicillin, an antibacterial agent of great potency against various pathogenic organisms such as *staphylococcus*, the *pneumococcus*, the *hemolytic streptococcus*, the *gonococcus*, and the *meningococcus*.

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[1] JENEMANN (to GRASSELLI Chemical Co.), U.S. Pat., 1906068 (Apr. 25, 1933).

[2] OLIVE, *op. cit.*, p. 483; here is given a pictured description of the Sheffield By-products Co., of Hobart and Norwich, N.Y., where under the direction of Dr. F. L. Chappell much of this work has been pioneered.

Penicillin[1] is obtained commercially by extraction of the filtered beer resulting from the action of selected strains of *P. notatum* on a mash of corn steep water and lactose. Sterile air must be supplied as this is an aerobic fermentation. The filtered beer has the penicillin concentrated by adsorption on activated carbon from which it is eluted and purified by appropriate organic solvents. The penicillin is finally extracted as the ammonium, sodium, or calcium salt in water, sterilized, and measured into small sterile bottles. In one process, this solution is frozen and the water evaporated from the ice under a very high vacuum. The product is then a dry substance all ready to be dissolved by the physician in sterile water and injected into the patient. The fermentation, isolation, and concentration are delicate steps because of the extreme sensitiveness of penicillin to contaminating organisms or to unfavorable chemical environment (see Fig. 10).

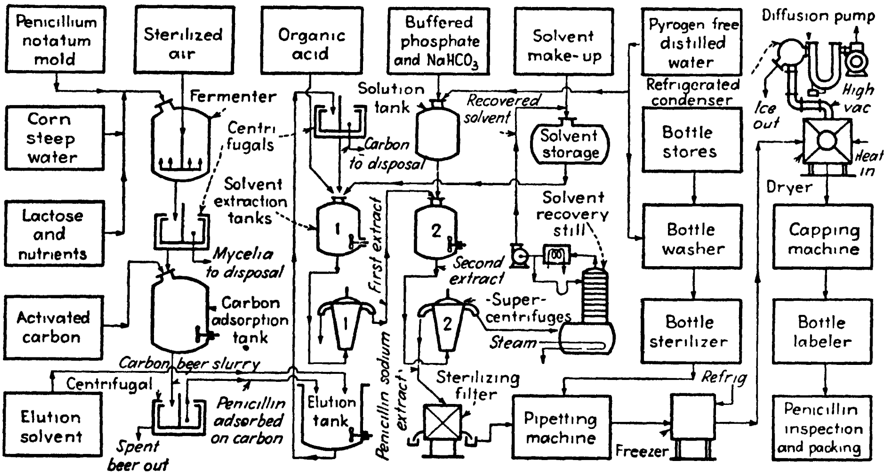

Fig. 10.—Penicillin flow sheet.

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CHAPTER XXXII

WOOD CHEMICALS

Wood, in general, may be divided into two classes, differing from one another in such physical characteristics as specific gravity, compactness of cell structure, and resistance to mechanical treatment, and in such chemical properties as lignin and resin content. These two classes are known as *hardwoods* and *softwoods*, or as broadleaf (deciduous) and coniferous woods. The former contain larger quantities of "extractive matter," including pentosans, while in the latter the amount of resinous matter present is high. Table 1 shows the average composition of wood, the values for the individual species falling within the ranges indicated. The resin content of the deciduous varieties is usually just high enough to cause difficulty but not high enough to yield any valuable product. Both types of wood (broadleaf and coniferous) are suitable for distillation to produce charcoal but, in the case of the resinous softwoods, prior extraction of oils and resins is desirable before the destructive distillation. However, commercial charcoal is made from hardwoods.

TABLE 1.—AVERAGE COMPOSITION OF WOOD[a]
(In per cent)

	Broadleaf or hardwood	Coniferous or softwood
Cellulose	56	58
Pentosans	18	7
Gums, resins, and oils	2	8
Ash	1	1
Lignin	23	26

[a] Adapted from Hawley, "Wood Distillation," Reinhold Publishing Corporation, New York, 1923.

DISTILLATION OF HARDWOOD

History.—The origin of the destructive distillation of wood can be traced back to antiquity. In ancient Egypt a process for the distillation of wood was known from which were recovered not only charcoal but fluid wood tar and pyroligneous acid as well. The latter was used for embalming. In early times, however, wood distillation was usually carried out for charcoal alone or, when resinous coniferous wood was used, for tar and pine oil in addition. At one time illuminating gas was manufactured from wood by the English, but the process was soon abandoned in favor of the now-familiar coal process.

Wood spirits, a mixture of acetic àcid and wood alcohol, was collected and purified to *wood alcohol,* as it was then called. The demands of the growing intermediate dye and synthetic organic chemical industries for wood alcohol became so great that wood was distilled for the main purpose of obtaining this solvent or reagent. In 1870, the process for the manufacture of acetic acid via calcium acetate from wood was developed. This caused marked advances in wood distillation processes all over the world, particularly in the United States and Hungary, where wood was cheap.

For many years the wood distillation industry was the chief source of acetic acid, methanol, and acetone. In addition it furnished considerable quantities of tar, pitch, methyl acetone, and wood oil to the trade. During the First World War, however, a process for producing acetone by fermentation was worked out, as described in Chap. XXXI. This process effectively removed the acetone produced by the pyrolysis of calcium acetate from wood distillation as a competitor. The introduction, in 1928, of acetic acid from calcium carbide and of acetone from propylene further decreased the wood distiller's market. The manufacture and importation from Germany of synthetic methanol a short time later were further shocks to this industry.

Now face to face with business ruin, wood distillers became conscious of the gross inefficiency of many of their operations and applied sound chemical engineering to their problems. Conditions improved immediately. Wood waste was used as a raw material rather than marketable timber. The drying time for the timber was shortened. Retort operation was made continuous, and processes for obtaining acetic acid directly were introduced.[1] Marketing of the charcoal produced[2] was greatly extended. With these improvements the industry not only has been able to survive but bids fair to continue as an important source of acetic acid, methanol, and charcoal.

Products and Economics.—During 1940, the hardwood distillation industry consumed about 540,000 cords of wood, producing therefrom 27,000,000 bu. of charcoal, the equivalent of 4,500,000 gal. of refined methanol, and 62,000,000 lb. of acetic acid or its equivalent. This indicated a per cord production of 50 bu. of charcoal, 10.25 gal. of crude or 8.33 gal. of refined methanol, and 115 lb. of acetic acid or equivalent. The methanol produced represented approximately 9 per cent of total production for the year, which was 49,470,000 gal., 44,970,000 gal. being manufactured synthetically.[1] The hardwood distillation industry is particularly important in the states of Pennsylvania, New York, Michigan, and Tennessee, where the wood is grown as a crop, being harvested after a sufficient period of years to furnish much merchantable timber, the scrap going into the retorts.

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[1] ALBIN, A Wood Chemical Plant Built to Meet the Competition of Synthetic Products, *Chem. & Met. Eng.*, **39**, 382 (1932); KIRKPATRICK, "Twenty-five Years of Chemical Engineering Progress," *Am. Inst. Chem. Engrs.*, pp. 35–42, D. Van Nostrand Company, Inc., New York, 1933.

[2] MCBRIDE, Chemical Engineering Problems in Hardwood Design, *Chem. & Met. Eng.*, **39**, 534 (1932).

The major items of plant cost per cord of wood processed are given in Table 2. It is interesting to note also that the cost of producing acetic acid as the free acid is approximately $1.47 per cord, as compared to the cost of producing it by the older, now-obsolete process, through calcium acetate, which was $2.95 per cord. The products from a cord of hardwood, on a weight basis, are distributed as shown in Table 3. These figures are based on air-dried wood and indicate an average yield of about 62.5 gal. of pyroligneous acid from 1,000 lb. of wood. Pyroligneous acid, the crude aqueous liquid distilling from the wood, contains the methanol and acetone as well as the acetic acid and much water.

TABLE 2.—COST PER CORD OF WOOD PROCESSED[a]

Item	Amount
Wood	$2–$7
Fuel equivalent	1,000 lb. bituminous coal (actually wood gas and tar are burned)
Labor	0.5–0.7 man-day
Water	12,000–15,000 gal.
Power	15 kw.-hr.
Capital investment	$4,000–$5,000 per cord capacity

[a] *Chem. & Met. Eng.*, **39**, 664 (1932).

TABLE 3.—PRODUCTS FROM ONE CORD (4,000 LB.) HARDWOOD[a]

Product	Per Cent
Charcoal	25.2
Crude methanol	1.9
Acetic acid, or equivalent	2.9
Tar, oil	5.0
Gas	18.3
Water, etc.	46.7

[a] *Chem. & Met. Eng.*, **39**, 534 (1932).

The products given in Table 3 have a wide variety of applications, some of which are described below:

Charcoal.—The chief uses of charcoal are as a blast-furnace fuel, a household fuel, and for miscellaneous metallurgical purposes. Considerable amounts are sold for carbon disulfide, carbon tetrachloride, and sodium cyanide manufacture. A list of the various uses, together with the percentage of the total production devoted to each has been published.[1]

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[1] *Chem. & Met. Eng.*, **48**, No. 2, 102 (1941).

Methanol.—This aliphatic alcohol is employed as a denaturant for ethyl alcohol, an antifreeze for automobiles, a solvent, a refrigerant, in the production of resins, and as a methylating agent.

Acetic Acid.—The applications of acetic acid are too numerous to mention completely. It is used in the preparation of a great number of the products of the process industries, including acetic anhydride, sodium acetate, cellulose acetate, ethyl acetate, butyl acetate, amyl acetate, white lead, and for dyeing.

Methyl Acetone.—This is a ternary azeotropic mixture of 21 per cent methanol, 28 per cent methyl acetate, and 51 per cent acetone and is sold as such by the refiners as a solvent to the paint and lacquer manufacturers. However, the composition in practice runs between the limits of 25 to 30 per cent methanol, 40 to 50 per cent acetic esters, and 25 to 45 per cent acetone.

Tar and Oil.—The tar produced yields pitch, useful as a rubber softener on electrical insulation, and widely sold gasoline oxidation inhibitor oils.[2] Various grades of wood oils are employed as solvents, in wood preservation, and as insecticides. Some are purified and redistilled to yield guaiacol and wood creosote. Any residue is burned under the plant boilers.

Gas.—The gas evolved contains 53 per cent carbon dioxide, 27 per cent carbon monoxide, and 15 per cent methane. It is burned to heat the retorts and to furnish part of the fuel for the boilers. It has an average heat content of 250 to 300 B.t.u. per cu. ft.[3]

MANUFACTURE

Raw Materials.—The hardwood distillation industry pyrolyzes all varieties of woods which are commonly classed as members of the broadleaf or deciduous species; *i.e.*, oak, ash, birch, beech, hard and soft maple, hickory, cherry, and chestnut. As stated previously, only wood wastes are commonly employed, *i.e.*, second-growth timber, branches, twisted trunks, and unmarketable lumber.

Energy Requirements, Unit Operations, Unit Processes.—The principal unit process is *pyrolysis* or destructive distillation. In this industry, although the pyrolytic reactions require considerable energy in the form of heat to reach the temperature of reaction, certain later stages are exothermic. Many unit operations are involved to make the unit process of pyrolysis function and to separate and purify the products of the pyrolysis. Among these are *heat transfer*, *condensation*, *distillation*, and *extraction* (*liquid-liquid*). Much energy is required to carry on these operations, mainly as steam. The modernization and improving of the wood distillation industry have largely been concerned with a chemical engineering study of the various unit operations involved in the separation and purification of the crude pyroligneous acid with the object of reducing cost, both capital and operating.

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[1] McBride, Marketing and Industrial Uses of Charcoal, *Chem. & Met. Eng.*, **39**, 664 (1932).

[2] Universal Oil Products Co., Chicago, Ill.

[3] Albin, *op. cit.*

Pyrolysis and General Treatments.—Except in the continuous retorts of the plant of the Ford Motor Co. at Iron Mountain, Mich., all United States plants producing wood chemicals by the destructive distillation of hardwood, char the wood in batches loaded on steel buggies on standard-gage railroad tracks, in steel retorts holding from 6 to 10 cords, operating on about a 24-hr. cycle. The retorts are hung in firebrick settings, heated by coal or natural gas, sometimes supplemented by the wood gas or tar obtained in the procedure of a previous batch. Some plants cut the wood into short blocks, some char 52-in. billets. Some predry wood for 2 or 3 days, using waste heat from retort or boiler furnace stacks; some dry wood out of doors for 3 to 18 months; but all produce about the same quality and quantity of charcoal and raw pyroligneous acid liquor (see Table 3).

Most plants settle and decant raw retort or pyroligneous liquor to separate clear liquor from settled tar, then give this clear decanted raw liquor a preliminary plain distillation to help free it from "soluble" or polymerized tar, thus producing so-called *boiled liquor*. A few plants, representing a small proportion of the total cordage pyrolyzed, still neutralize acids in boiled liquor with lime, distill off "weak alcohol" from this neutralized liquor, and evaporate to dryness the remaining acetate liquor to produce "gray" calcium acetate. (One small plant makes sodium acetate.) Most plants distill methanol continuously from boiled liquor, but some demethanolize raw decanted liquor.

Acetic Acid Separation and Purification.—The greatest differences in the processes are in the methods of concentration or recovery of acetic acid. Some small quantities of gray calcium acetate are still shipped in bags to converter plants, where this product is heated with sulfuric acid to recover 80 per cent crude acetic acid which must be refined. At least two plants make acetic esters directly from wood liquors without concentrating the acid. One 60-cord wood chemical factory in the United States removes the acetic acid by the azeotropic distillation process described in this chapter and depicted by Fig. 3. Two plants employ the Suida process. All the rest use liquid-liquid countercurrent cold-solvent extraction, with ethyl ether or ethyl acetate.

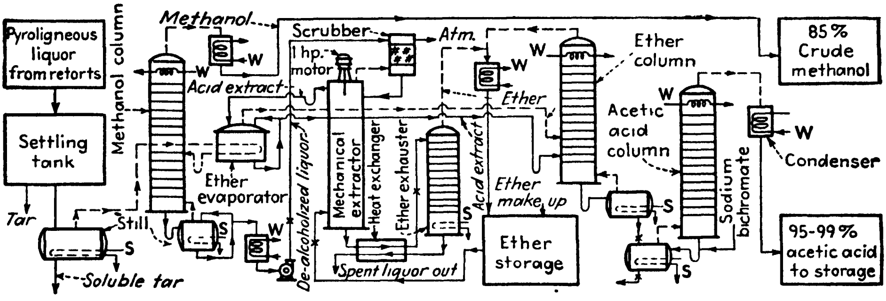
The first cost of the wood distillation portion of the *lime process* equipment is low, but the final cost of acid is high and is justified only by exceptionally low wood and fuel costs, high product prices, or very short prospective factory operation. Hardwood liquor from which methanol has been removed is about 90 per cent water. The lime process must distill this liquor twice: once in the primary stills and again to dry and crystallize acetate of lime. The steam consumption is therefore quite high. Sulfuric acid is also required for decomposition of the calcium acetate to 80 per cent crude acetic acid, which must be refined also. In consequence of all these factors, the calcium acetate process for acetic acid is on the decline.

Liquid-liquid Extraction Process.—The liquid-liquid extraction process, as illustrated by Fig. 1, seems to be favored because, in a single continuous cold treatment with solvent, substantially all the acetic acid is extracted from the liquor with over 95 per cent of the water content flowing to waste without the necessity of reevaporating it. The choice between the two commonly used solvents, ethyl ether and ethyl acetate, depends largely on local fuel costs. Ethyl acetate produces a somewhat drier extract and its vapor pressure is lower, with consequent less tendency to solvent loss. Since density, latent heat of vaporization, and boiling temperature are all greater than for ethyl ether and since about the same *volume* of each is required, steam consumption is considerably lower for the ether. Further, the greater temperature difference between the boiling points of boiled liquor and ether allows the economical use of liquor vapors from primary stills in an evaporator for the evaporation of ether after extraction (see Fig. 1). Thus the advantage of low steam consumption is greatly in favor of ethyl ether. In properly designed and operated acetic extraction plants, ether losses can be kept under 1½ lb. per cord, thus providing a very satisfactorily low solvent cost of 5 to 8 cents per cord. Isopropyl ether has been considered as an extraction solvent, but the relatively unfavorable acetic acid distribution coefficient makes the other solvents more economical.

Aside from the choice of solvents, the major differences in extraction plants are in the types of extractors used. Most ethyl acetate plants employ a modified bubble-plate column extractor. Most ether plant extractors are single columns equipped with mechanical mixing, distributing, and agitating devices extending throughout the length of the column. They have proved very dependable and efficient; *i.e.*, the solvent attains very nearly its theoretical maximum acid concentration in contact with feed liquor of any given concentration, thus necessitating the circulation of a minimum amount of solvent.

Ether extraction has been called the *Brewster process* for T. J. Brewster, who early did small-scale pilot-plant work, then designed one large commercial plant which was built and after many months of experimenting failed. The development and design by J. M. Coahran[1] of new extractors to increase yield, and the introduction of heat economies, means, and procedures to minimize ether losses, made the process practical.

Figure 1 is a flow diagram of a typical plant for *ether extraction* of acetic acid from pyroligneous acid liquor. Very little alteration of such a plant would be necessary to make it suitable for use with any appropriate solvent. This process may be broken down into the following coordinated sequences of *unit operations* (Op.):



Key: **S** = Steam; **W** = Water; ------Vapor; ——— Other process fluids

Whole raw liquor from 1 cord hardwood 250 gal.
Solvent ether loss $1\frac{1}{2}$ lb.

Steam	940 lb.	Per 120 lb refined acetic acid (basis 100%) and 8 5 –10 gal crude methanol (basis 100%)
Water	6,000 gal.	
Direct labor	0 4 man-hr	
Depr. 10%, Maint., etc., 40c		

FIG. 1.—Acetic acid by cold liquid-liquid extraction from pyroligneous acid. (*Courtesy of J. M. Coahran.*)

Settled raw liquor (pyroligneous acid after settling out of the insoluble tar) is fed continuously to a primary still for distillation from the soluble tar in order to lessen fouling of subsequent operations (Op.).

Mixed vapors from this still are passed to the heater tube bundle of the ether evaporator and, after partial condensation, to the middle of the methanol column as its feed. Eighty-five per cent crude methanol is the overhead from this column, and dealcoholized liquor is the bottom discharge (Op.).

The latter is cooled and pumped through a vent scrubber into the upper part of the mechanical countercurrent extractor (Op.).

The acetic acid in the dealcoholized liquor is extracted *cold* as the aqueous liquid passes downward in this mechanical extractor, using 2.6 volumes of ether per volume of liquor countercurrent to the rising ether (Op.).

The ether-saturated extracted liquor is conducted through a heat exchanger to the top of a steam-heated ether exhauster column for the recovery of the dissolved ether. The spent liquor flows from the bottom of this exhauster through the heat exchanger to waste, containing less than 0.1 per cent acetic acid (Op.).

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[1] COAHRAN, U.S. Pats. 1680452 (Aug. 14, 1928); 1784270 (Feb. 9, 1930); 1845128 (Feb. 16, 1932); 1845129 (Feb. 16, 1932); 1865887 (July 5, 1932); 1870834 (Aug. 9, 1932); 2197069 (Apr. 16, 1940).

The ether solution of the acetic acid (2 to 3 per cent) is piped from the top of the mechanical extractor to the ether evaporator. Here, heated by the vapors from the primary still, the ether is vaporized, along with some acetic acid (Op.).

The acid freed of most of its ether is led to a lower section of this same ether column. The overhead is rectified ether vapor to be condensed and recirculated. The discharged acid collects in an acid extract receiver kept sufficiently warm by steam to remove ether (Op.).

The ether has carried over into this acid extract practically all of the acetic acid, a small amount of wood oils, some polymerized tar, and from 2 to 3 per cent of water—resulting in a 70 per cent dark crude acid. The water content is a distinct advantage as it forms minimum boiling mixtures with the volatile impurities and facilitates their fractional separation. If sufficient water is not present, it is expedient to add it.

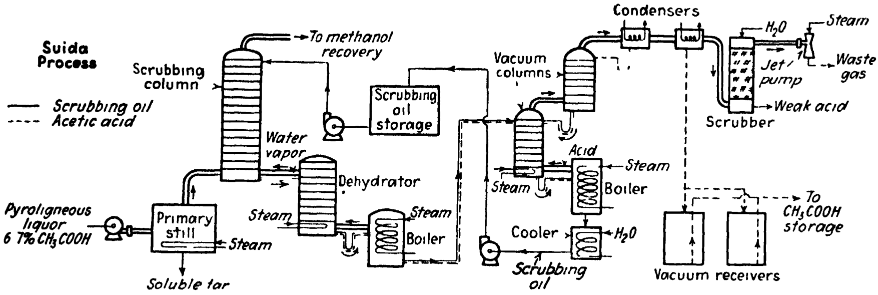
The 70 per cent crude acetic may be refined by either continuous or batch distillation. Figure 1 shows a single batch distillation with an oxidizing and purifying treatment with from 2 to 4 lb. of sodium dichromate per ton of acid. Sometimes, double distillation is practiced with the dichromate treatment between (Op.).

The final acetic acid is of any desired concentration from 90 per cent to glacial, of water color, and with a purity dependent upon the design of the fractionating equipment and the care with which it is operated. Final acid condensers are usually constructed of silver, though aluminum or Duriron can be and sometimes is used. Other acid-handling equipment is made of copper or copper alloy, and the parts handling strong hot acid are often lined with acidproof brick set in acidproof cement. Strong acid is stored and shipped in aluminum or wooden tanks, with an occasional rubber-lined vessel.

Suida Process.—In the Suida process (Fig. 2) the upper layer from the initial settling of the crude pyroligneous acid is first treated to remove acetic acid by being vaporized and scrubbed countercurrently with a wood oil, which is obtained by vacuum distillation of the tar from the settlers (see Fig. 1). The oil with acetic acid in solution passes through a dehydrating column into a vacuum stripping column, where the acetic acid is boiled off under vacuum. The oil returns to the system, while the acetic acid is rectified to 92 per cent or higher. Fresh oil is added to the scrubbing column at frequent intervals. The vapors from the scrubbing column, having been stripped of acetic acid by the oil, are sent to methanol recovery, their alcohol content being about 4 per cent. They also contain a small amount of acetone. Subsequent concentration in an exhausting and rectifying system produces 90 per cent methanol or its equivalent. Final rectification yields 99 per cent methanol, allyl alcohol, acetone, and "weak alcohol." The yields of products per cord (4,000 lb.)

of wood and resulting 250 gal. of pyroligneous acid are charcoal, 1,330 lb.; oil, 4.5 gal.; tar, 40 to 45 gal.; acetic acid (100 per cent basis), 120 lb.; and methanol (100 per cent basis), 9 gal.[1]

The first cost of the Suida process equipment is large because the scrubbing column must handle so much water vapor, and the remaining equipment must be heavy to withstand the vacuum under which it operates. High-pressure, high-temperature steam is required to distill tar under vacuum to produce the high-boiling scrubbing oil employed to recover acetic acid. The process is well developed and the yields are among the very best, but it has not been extensively installed in the United States, probably because of the comparatively excessive steam costs.



Pyroligneous liquor	17 tons	Water (including retorts)	240 M gal	Per ton 100% acetic acid
Scrubbing oil	500-600 lb	Electricity	25 kw-hr	
Steam	32-37 tons	Direct labor (incl maint)	12 man-hr	

FIG. 2.—Flow sheet for acetic acid extraction from pyroligneous liquor—Suida process.

Othmer or Azeotropic Distillation Process.—The various steps may be divided into the following *unit operations* (Op.) and *unit processes* (Pr.):

Hardwood, previously dried so that moisture content is about 25 per cent, is loaded on "buggies," which hold about 2 or 2½ cords of wood, rolled into a steel retort 50 to 55 ft. long, and heated for about 20 hr. at 600 to 700°F. (Pr.). In order to avoid warping, the doors of the retort are not heated. The initial temperature may be maintained at about 500°F. for 4 hr. to distill out the water, and then raised to 700°F. for 4 to 6 hr. more. At the end of this time the reaction becomes exothermic and little or no external heat is needed to maintain the desired temperature.

Charcoal is removed from the retorts and cooled out of contact with air for 48 hr., placed in open sheds for 2 days, and shipped to consumers (Op.).

The vapors formed by the heat-treatment are passed through water-cooled copper condensers (Op.).

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[1] POSTE, Suida Process for Acetic Acid Recovery, *Ind. Eng. Chem.*, **24**, 722 (1932); KRASE, Solvent Extraction Obviates Waste in Acetic Acid Production, *Chem. & Met. Eng.*, **36**, 657 (1929); also PERRY, *op. cit.*, pp. 1256–1264, for data on the efficiency of various solvents for the extraction of acetic acid.

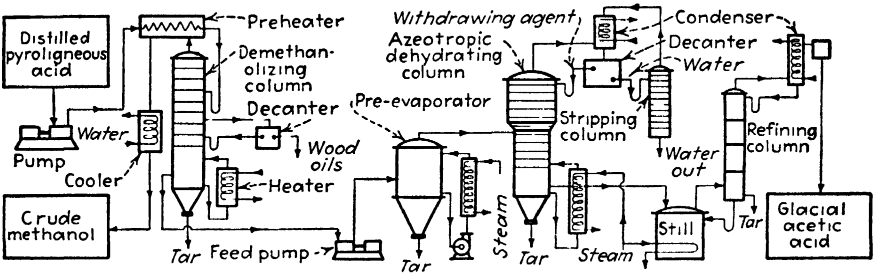
The wood gas produced is conducted to a scrubbing system and sent to the distributing pipes leading to the burners (Op.). The gas has a fuel value of 290 B.t.u. per cu. ft.[1]

The condensed vapors, known as *pyroligneous acid* or liquor, are sent to settling tanks for 24 hr. Here the insoluble tars settle out and are removed (Op.).

To remove the soluble tar, the raw settled pyroligneous acid is distilled in a primary tar still[2] (Op.).

Liquid from the tar still is pumped to the demethanolizing column and the crude methanol distilled (Op.). This distillation is a continuous operation. The plates in the column below the feed plate are of a special perforated design to permit removal of tar deposits (see Fig. 3).

"Crude methanol," containing some acetone and methyl acetate and about 15 per cent water, is fractionated off the top of the column and condensed (Op.).



Wood	1cd, 4,000 lb	Withdrawing agent	015 lb	Per 115-120 lb acetic acid, 10-12 gal crude methanol, 25-26 gal tar and approx 50 bu charcoal or 1,000 lb, and 7,000 cu ft wood gas
Steam	3,250 lb	Sodium bichromate	2 lb	
Electricity	4 Kw.-hr	Labor	1/3 man-hr.	

FIG. 3.—Direct acetic acid by azeotropic distillation—Othmer process.

Dealcoholized liquor from the bottom of the column is metered and sent to a preevaporator (Op.). This evaporator has a conical bottom to permit removal of the tars that passed the previous treatments.

The remaining volatile materials (acetic acid and water) are distilled in the evaporator, pass through a catchall to remove any suspended matter and then to the azeotropic dehydrating column (Op.). Water cannot be removed practically from acetic acid by simple distillation because of the excessive number of plates required in the column and the prohibitive heat requirements. The water is removed in the dehydrating column by adding a water-insoluble "withdrawing" liquid such as butyl acetate.[3] This method of removing water from acetic acid is the Othmer process. Ethylene chloride or ethyl tertiary amyl ether may also be used for this purpose. The butyl acetate distills with the water as a minimum boiling azeotrope and thus removes the water from the acid (Op.).

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[1] POSTE, *op. cit.;* MCBRIDE, Chemical Engineering Problems in Hardwood Design, *Chem. & Met. Eng.*, **39**, 604 (1932).

[2] Although this step was not in the original setup of the plant, it was found necessary to interpose it to avoid fouling of the heater of the preevaporator. Naturally, this increased the steam consumption. For removal of tar by treatment with sulfuric acid, see Othmer and Katzen, Tar Elimination in Pyroligneous Acid, *Ind. Eng. Chem.*, **35**, 388 (1943).

[3] OTHMER, Acetic Acid and a Profit from Wood Distillation, *Chem. & Met. Eng.*, **42**, 356 (1935); OTHMER, Dehydrating Aqueous Solutions of Acetic Acid, *Chem. & Met. Eng.*, **40**, 631 (1933), Pictured flow chart, *Chem. & Met. Eng.*, **47**, 349 (1940).

The vapors of butyl acetate and water are condensed and cooled. Separation into two layers takes place (Op.).

Butyl acetate is returned to the top plate of the column and the water containing a small amount of butyl acetate is distilled to recover all of the acetate (Op.). The water discharges from the bottom of this water column and contains less than 0.01 per cent acetic acid.

The crude acetic acid from the dehydrating column contains some propionic and butyric acids, a little tar, and about 0.5 per cent water. This is rectified in a column or batch still and sometimes in two columns to produce glacial acetic acid. The introduction of sodium dichromate into the still is practiced to remove all empyreumatic substances.

The steam consumption of the azeotropic distillation process, as operated, is high because of the necessity for two complete evaporations of all the wood liquor; once in primary stills to remove soluble tar and again in the preevaporator feeding the dehydrator column, as shown in Fig. 3. Also the heavy reflux and the high ratio between withdrawing agent and water in this column increase the steam requirements. The azeotropic column is necessarily quite large and expensive because it handles so much liquor and withdrawing agent vapor.

Continuous Hardwood Distillation.—The plant of the Ford Motor Company at Iron Mountain, Mich., varies from the previously described processes not only in methods of operation but also in the products. Dry wood is fed to Badger-Stafford retorts at 302°F., entering at the top and being heated as it sinks, until it distills. Retort temperature is 1004°F., maintained (after initial heating of the retort to this point by gas) entirely by the exothermic reaction accompanying distillation. These retorts, which are 40 ft. high and 10 ft. in diameter, discharge into rotary coolers lined with water-cooled tubes and externally sprayed with water. From the coolers the charcoal passes to rotary conditioners, which permit absorption of oxygen. Complete conditioning of the charcoal in 5 hr. is possible by this method.[1]

The wood gas and pyroligneous acid are taken off the retorts and the acid is condensed. The gas is scrubbed and used for fuel. Every two weeks the stills are taken off the line, and the tar is removed. This latter is sent to the pitch department where creosote oil and pitch are recovered. The pyroligneous acid is settled to remove tar.

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[1] NELSON, Waste-wood Utilization by the Badger-Stafford Process, *Ind. Eng. Chem.*, **22**, 312 (1930). RIEGEL, "Industrial Chemistry," 4th ed., pp. 276–277, Reinhold Publishing Corporation, New York, 1942, gives a flow sheet for this process.

The Ford plant produces various esters of acetic acid and not the free acid as its products. The distillate from the primary tar stills is distilled in a continuous system to yield 95 per cent *crude* methanol overhead and 15 per cent acetic acid at the base of the column. The crude wood alcohol, containing allyl alcohol, methyl acetate, and acetone, is refined in discontinuous stills, yielding refined allyl alcohol in addition to several fractions that yield pure methanol, 75 per cent methyl acetone, and 75 per cent methyl acetate upon further refining. The 15 per cent acetic acid initially obtained is esterified to ethyl acetate.

PRODUCTS FROM SOFTWOOD

The term *naval stores* is usually applied to the group of products made by the distillation or extraction of softwood or from the oleoresin that exudes therefrom. These products are turpentine, rosin, pine oil, rosin oil and spirit, pine tar, and pitch. These products were used by the Navy in the days of wooden ships. Turpentine and rosin are complex mixtures of organic compounds obtained from pine wood or sap. Four processes are available for the production of both turpentine and rosin, as shown in Table 4. The destructive distillation of wood yields turpentine but does not produce rosin, while reclaimed gum residues yield rosin but no turpentine.

History.—Turpentine and rosin are produced from the longleaf pine. This tree flourishes particularly in the Southeast and Southern parts of the United States; in fact, in the early days of America the forests in this region were said to extend in a belt approximately 200 miles deep and 1,000 miles long. The earliest records show that turpentine was being made in 1606 in Maine. In 1608 what was probably the first cargo of American naval stores was shipped to England. Pine tar manufacture became one of the first industries of the New England colonies, flourishing as early as 1650.[1] By 1750, North Carolina had been settled and had established a growing trade in naval stores. In 1770, the state exported 88,000 bbl. of turpentine and a similar amount of "tar" or rosin. During the early 1800's, turpentine came into prominence as the *major* commodity. By 1860, South Carolina, Georgia, and Florida had begun production and by 1900 Georgia was the chief producing state. The same year, H. T. Yaryan of Toledo, Ohio, began a series of experiments which resulted in the erection of a plant at Gulfport, Miss., to obtain turpentine and pine oil from the logging waste and also to attempt the removal of the rosin present. Plant production by the steam distillation method rose to 1,700 bbl. of turpentine, 14,000 bbl. of rosin, and 700 bbl. of pine oil per annum. Meanwhile, supremacy for producing crude turpentine had been captured by Florida. In 1913, the Newport Company began operations, to be followed by the Makie Pine Products Company in 1918 and the Hercules Powder Company in 1920. All used the steam and solvent process. By 1920, North and South Carolina were making less than 1 per cent of the total turpentine production of the United States and, by 1933, Georgia and Florida were accounting for 85 per cent of the gum turpentine and rosin produced. Meanwhile, the steam and solvent industry continued to grow and improve, until today this process produces 20 to 25 per cent of the total turpentine and rosin made in the United States.[1] The industry has offered countless new products and grades of old products to the consumer and promises to continue to do so.

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[1] Palmer, Naval Stores, *Ind. Eng. Chem.*, **27**, 741 (1935).

Products and Economics.—The production of rosin and turpentine during the 12-month period from April, 1938, through March, 1939, is shown in Table 4. The apparent United States consumption during this same period was 21,000,700 gal. of turpentine and 584,363,500 lb. of rosin. Thus, the United States consumed approximately 60 per cent of its total domestic production of turpentine and about 45 per cent of its rosin production. During the year 1939 the United States production of pine oil totaled some 5,198,696 gal. "Gum" turpentine or rosin refers to that obtained by exudation from incisions in trees of the longleaf or slash-pine varieties, while "wood" turpentine or rosin indicates the same products from destructive distillation, steam distillation, or extraction of *wood* or stumps.

TABLE 4.—UNITED STATES PRODUCTION OF ROSIN AND TURPENTINE, 1939[a] AND 1941[b]

	Turpentine, gallons		Rosin, pounds	
	1939	1941	1939	1941
Gum	26,714,550	14,252,500	896,475,500	484,819,000
Reclaimed (gum)	....	....	14,989,500	
Steam-distilled wood	6,454,550	13,187,300	381,456,500	572,977.500
Sulfate wood	2,023,350	....	8,274,000	
Destructively distilled wood	268,450			

[a] ANON., *Chem. & Met. Eng.*, **47**, No. 2, 91 (1940).
[b] ANON., *Chem. & Met. Eng.*, **50**, No. 2, 121 (1943).

Although turpentine and rosin are available from four different methods of production as shown in Table 4, the uses of each product from the various sources are generally interchangeable; hence, no attempt will be made to distinguish between these sources in the list that follows. The major products[2] of the naval stores industry are the turpentines, rosins, pine oils, rosin oils, spirits, and pine tar pitches and tars. The tabulation at the bottom of Fig. 4 shows the products obtained from 1,000 tons of white pine chips, while Table 5 represents the consumption of turpentine and rosin in various industries.

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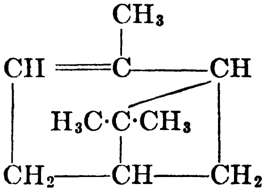
[1] GARVIE, The Wood Naval Stores Industry, *Chem. Age*, **39**, 387 (1938).

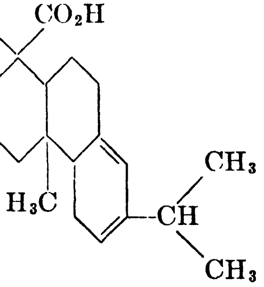
[2] SPEH, Utilization of Naval Stores, *Ind. Eng. Chem.*, **31**, 166 (1939); PALMER, Solvents from Pine, *Ind. Eng. Chem.*, **35**, 1023 (1943).

Turpentine is a mixture of organic compounds known as *terpenes.* The principal constituent is α-pinene:



The outstanding use of turpentine as a paint and varnish thinner accounts for a large part of the present consumption. In addition, it is widely used as a solvent for waxes and polishes of various sorts (10 per cent), as a solvent, as an ingredient of insecticides, and for household purposes. Its future market lies in the chemical field, where turpentine is a raw material for such products as synthetic camphor and terpineol, as well as pharmaceuticals.

Rosin.—One of the chief components of rosin is abietic acid (probably the anhydride),



although other acids such as α- and β-pimaric also are present. Many grades of rosin[1] are on the market, largely distinguished by color, clarity, saponification number, and softening point.

The paper and paper-sizing industry consumes over a third (370,000 bbl. per year) of the present annual total consumption of rosin, principally as a size for paper. The soap industry uses approximately one fourth, while about one fifth goes into the manufacture of the cheaper varnishes. Cobalt, manganese, and lead resinates are used as driers.

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[1] "Rogers' Manual of Industrial Chemistry," 6th ed., Chap. 17, p. 691, D. Van Nostrand Company, Inc., New York, 1942; HUMPHREY, Solvent Refining of Wood Rosin, *Ind. Eng. Chem.*, **35**, 1062 (1943).

Rosin enters into insecticides and germicides because of its adhesiveness, a property that enables it to be used in such widely diversified products as can label cement, linoleum, and sealing wax. The esters of rosin are also quite useful. Methyl and ethyl abietates are employed as plasticizers and cosolvents, while the glycerol ester, widely known as *ester gum,* is applied with tung oil in making water-resistant varnishes. Ester gum is important in synthetic resin and nitro-cellulose coatings.

TABLE 5.—CONSUMPTION OF TURPENTINE AND ROSIN BY VARIOUS INDUSTRIES IN 1941[a]

Turpentine

	Quantity, in 50-gal. barrels	Per cent distribution
Paints, varnishes, lacquers	29,090	40.8
Chemicals and pharmaceuticals	31,907	44.8
Shoe polish and materials	4,424	6.2
Railroads and shipyards	3,763	5.3
Foundries	546	0.7
All other industries	1,569	2.2
Total	71,299	100.0

Rosin

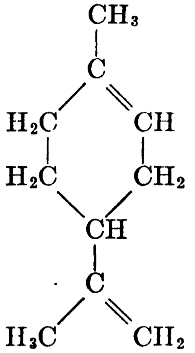
	Quantity, 500-lb. barrels	Per cent distribution
Paper and paper size	209,598	27.8
Soap	126,240	16.7
Chemicals and pharmaceuticals	71,818	9.5
Paints, varnishes, lacquers	128,605	17.2
Ester gums, synthetic resins	116,054	15.6
All other industries	98,069	13.2
Total	750,384	100.0

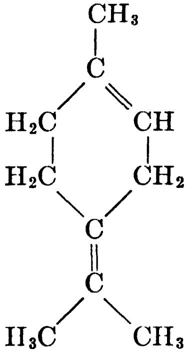
[a] ANON., *Chem. & Met. Eng.*, **49**, No. 2, 102 (1942). For the period April, 1941, through March, 1942. Much unreported, reaching consumption through retail and export channels.

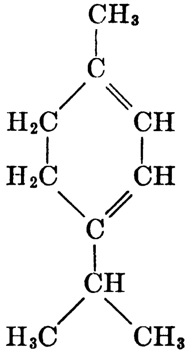
Rosin Oils.—These oils are used in printers' inks and in varnishes. They are rather high-boiling oils obtained by destructively distilling rosin and are of higher molecular weight and of greater chemical complexity than the terpene hydrocarbons.

Pine Oils.—These are mixtures of terpene alcohols, terpenes, aldehydes, and ketones. They do not occur naturally but arise by distillation of wood. They have been fractionated to yield α-terpineol, fenchyl alcohol, borneol, and anethole. Industrially, pine oil itself is used in the flotation of lead and zinc ores, as a solvent in rubber recovery, in textile scouring, and as a cleanser, disinfectant, and deodorant.

Dipentene.—Commercial dipentene is a mixture of dipentene (or limonene), terpinene, and terpinolene. These compounds are isomeric *p*-terpadienes.


Dipentene


Terpinolene


α-Terpinene

Dipentene is a solvent, widely used because of its ability to prevent, or at least retard, the formation of surface skins in cans of paint, printing ink, or varnish. It is also employed as a solvent in reclaiming rubber from old tires.

Manufacture.—The *raw materials* for the production of naval stores include those species of wood commonly classed as coniferous. Either the gum that flows from the living longleaf or slash pine, or the stumps from the cutover pine forests, together with other resinous wood wastes, form the source of raw material for the various processes employed.

Gum Turpentine.—Longleaf and slash pine are "chipped" and the resulting flow of gum is collected. This oleoresin, essentially a solution of rosin acids in turpentine, is charged to a copper still, usually of 25 bbl. capacity, and distilled. The distillate, turpentine and water, is collected and separated by gravity and the resulting product barreled. The rosin in the still is filtered and run into vats. It is then barreled in glued stave barrels and allowed to harden. Each pound of gum yields 0.2 lb. of turpentine and 0.8 lb. of rosin. Some plants filter the hot rosin through cotton batting and then extract it with naphtha. This naphtha solution is distilled to remove the solvent, thus furnishing the pine rosin.

Destructively Distilled Wood Turpentine.—This product involves a distillation very similar to that employed for the distillation of hardwood. The pine wood is charged to gas-fired retorts arranged in long rows. The vapors and gases pass through condensers and drain into open tubs. The noncondensable gases are used for retort fuel. The heating period is 16 hr. and the cooling period 8 hr. The lighter oils are condensed first and separated from the pyroligneous liquor which settles to the bottom. During the latter half of the run, heavier oils come over and displace this acid which rises to the top. The light and heavy oils are filtered, treated, and combined for redistillation in pot stills. This latter is a steam distillation, the distillate containing turpentine, pine oil, and dipentene. The mixture is bleached with sulfuric acid and subsequently fractionated and refractionated to produce refined dipentene, refined turpentine, and pine oil.[1] The residue in the original pot stills is pine tar. No rosin is produced.

Steam and Solvent Turpentine.—The cutover pine forests of the South have provided the raw material for the most recent source of turpentine. This is the stumps and other resinous waste wood, which contain approximately 20 per cent of extractable materials.[2]

Figure 4 shows the essential *unit operations* (Op.) in the production of turpentine, rosin, and pine oil by this method.

The wood is first ground in a wood hog and then reduced to splinters in a shredder (Op.).

The chips are loaded into a battery of extractors, where they rest upon a false bottom, below which live steam under pressure is admitted at the end of the run for solvent recovery.[3] The extractors are built of acid-resistant stainless alloys (Op.).

The solvent (so selected that it is easily separated from turpentine) countercurrently extracts the chips (Op.). This solvent may be naphtha or a not too volatile cut of gasoline.[4] The hot solvent is drained off, and the residual material on the chips is removed by subsequent steam distillation[5] (Op.).

The chips are used for fuel (Op.). One or two plants are attempting to utilize these chips in the manufacture of building board[6]

Most of the solvent is removed from the turpentine, pine oil, and rosin in a concentrating evaporator (Op.).

The residue from the first evaporator is sent to an intermediate evaporator. The vapors from this evaporator are led into the upper part of the continuous fractionating column, and the residue is sent to the finishing evaporator (Op.).

Vapors from this final evaporator are combined with those of the intermediate evaporator before entering the fractionating column (Op.).

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[1] NEALEY, Distilling Pine Products at New Orleans, *Chem. & Met. Eng.*, **43**, 20 (1936).

[2] GARVIE, *op. cit.*

[3] HANCOCK and KAISER, Purification of Wood Rosin, *Ind. Eng. Chem.*, **22**, 446 (1930).

[4] PALMER, Pine Stumps to Fine Chemicals, *Du Pont Magazine*, **31**, No. 4, 18 (1939). For a pictured flow chart, see *Chem. & Met. Eng.*, **49**, No. 3, 172 (1942).

[5] PALMER, Producing Naval Stores from Waste Wood, *Chem. & Met. Eng.*, **37**, 289 (1930).

[6] PICKETT and SCHANTZ, New Uses of Naval Stores Products, *Ind. Eng. Chem.*, **26**, 707 (1934).

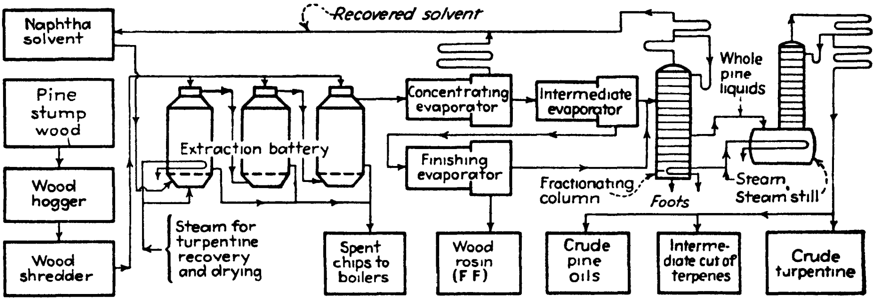
Residue from the third evaporator is whole wood rosin and may be treated by selective solvents and filtered through fuller's earth to separate it into dark and light rosins[1] (Op.).

The continuous fractionating column separates the pine oils and turpentine from the last of the solvent (Op.).

Pine liquids from the continuous column are separated into three fractions in a batch still: crude pine oil, an intermediate cut of terpenes, and crude turpentine (Op.) (see Table 5).

Careful fractionation of these three cuts produces many marketable products (Op.).

Sulfate Pulp Turpentine.—The relief gases from the digesters for sulfate (or kraft) pulp contain turpentine and pine oil. Upon condensation, a crude oil is found floating on top of the condensate. There are 2 to 10 gal. of oil per ton of pulp produced. This oil contains 50 to 60 per cent turpentine and 10 to 20 per cent pine oil; and these may easily be separated by fractional distillation. The resulting turpentine contains offensive mercaptans which must be removed by hypochlorite solution or ethylene diamine.[2] Another by-product of the process is tall oil, a so-called *liquid* rosin obtained upon acidification of the digester liquor. It might be classed as a sulfate rosin.



Turpentine	155-167°C	5,270 gal	Pine oils	5,000 gal	Obtained from 1,000 tons of white pine
Intermediate terpenes*	167-200°C	2,700 gal	Tar	540 gal	
			Total crude oils	13,510 gal	

*Included herein are the hydrocarbons para-menthane, dipentene, para-cymene, terpinene, and terpinolene

FIG. 4.—Flow sheet for wood rosin and turpentine by steam and solvent extraction.

"Sulfite turpentine" is another kind of turpentine available from the paper industry and consists chiefly of *p*-cymene rather than of α-pinene. It is obtained from the pulping of spruce by the sulfite process. From

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[1] PICKETT and SCHANTZ, *op. cit.;* SCHANTZ and MARVIN, Waste Utilization, *Ind. Eng. Chem.*, **31**, 585 (1939); "Rogers' Manual of Industrial Chemistry," 6th ed., p. 692; HUMPHREY, Solvent Refining of Wood Rosin, *Ind. Eng. Chem.*, **35**, 1062 (1943).

[2] "The Manufacture of Pulp and Paper," vol. III, 3d ed., sec. 5, p. 192, McGraw-Hill Book Company, Inc., New York, 1937.

0.36 to 1.0 gal. are obtained per ton of pulp. The potential supply is 1,500,000 to 2,000,000 gal. per year.[1]

* * * * * *

The increased use of chemicals from wood is dependent upon a solution of the problem as to what their various chemical components are. This is being solved and new derivatives are being made; such a result is stimulating to the entire naval stores industry. *There is ample evidence to predict that the component products of this industry can be developed by research to form the basis for a group of allied industries similar in interdependence to coal tar and its related drug and dye industries.*

HYDROLYSIS OF WOOD

The possibility of converting the cellulose in wood to fermentable sugars has been the subject of many investigations, but only recently have any successful commercial processes been evolved.

History.—The saccharification of wood received its first industrial trial at the beginning of the present century. In 1910 Ewen and Tomilson erected a plant for the recovery of alcohol from sawmill waste, at Georgetown, S.C. Dilute sulfuric acid was the hydrolyzing agent. The plant was closed down after some time because of low yields. At the same time Scholler was trying to produce alcohol from wood in Germany. Using about the same methods, he attained yields of a 3 per cent sugar solution, representing 60 to 70 per cent of theory. This same year, Willstätter and Zechmeister published the discovery that, at ordinary temperatures, 40 per cent hydrochloric acid easily dissolves cellulose. It was not until 1916, however, that Bergius and Haaglund undertook the development of a process employing hydrochloric acid and not until 1930 that Scholler began operations with sulfuric acid at Tornesch.[2]

Products and Economics.—The hydrolysis of wood might ultimately yield such products of wood distillation as acetic acid, methanol, and wood sugar. The latter can be fermented to alcohol, used as a source of yeast and glucose, or consumed as a cattle food. Thus, wood hydrolysis has the advantage that much of the wood ordinarily converted to carbon dioxide and water in distillation is utilized by being converted to wood sugar. In addition, the process provides a means for utilizing wood waste —sawdust, shavings, wood taps, raspings, and low-value residues. The lignin obtained has been put to a variety of uses, including lignin plastics[3]

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[1] Mann, Sulfite Turpentine, *Ind. Eng. Chem.*, **28**, 598 (1936).

[2] Bergius, Conversion of Wood to Carbohydrates, *Ind. Eng. Chem.*, **29**, 247 (1937); Bergius, The Utilization of Wood for the Production of Foodstuffs, *Trans. Inst. Chem. Engrs.*, **11**, 162 (1933).

[3] John, Research and Development in the Chemical Utilization of Waste Wood, *J. Forestry*, **35**, 1102 (1937).

(both by partial hydrolysis and by combination with sulfur), for the production of charcoal briquettes, and in vanillin production.

No commercial data are yet available for the production cost for alcohol via either the Scholler or the Bergius process. These processes for alcohol are unlikely, however, to compete in America with alcohol from molasses, petroleum, or grain unless salable by-products are obtained. If fodder or yeast is prepared by the above hydrolysis processes, the necessary market price will be very unfavorable in comparison to the present prices of brewery yeasts and fish or meat meal. In the United States it is not economical *at present* for the wood-sugar industry to exist.

Manufacture.—In Germany there are two processes for the saccharification of wood capable of being used industrially. These are the Bergius process, employing 40 per cent hydrochloric acid, and the Scholler process, using a 0.2 to 0.6 per cent sulfuric acid solution. The former is highly successful, technically, but is commercially of less interest than the latter.[1] The details of these processes can be found in the references given in the footnotes. The making of wood sugar and alcohol therefrom is being experimented with in a large way by the Office of Production, Research and Development of the War Production Board in coordination with the United States Forest Products Laboratory and others. Reports have already been published[2] which deal principally with the hydrolysis of the cellulose with dilute sulfuric acid at high temperatures.

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[1] ANON., Sugar and Alcohol from Cellulose, A Comparison of the Scholler and Bergius Processes, *Chem. Age*, **23**, 521 (1933). Flow sheets are given in Riegel, *op. cit.*, pp. 287, 289.

[2] SHERRARD, FAITH, *et al.*, Symposium on Sugars from Wood; eight papers on various phases with full bibliographies, *Ind. Eng. Chem.* **37**, 4–54 (1945).

CHAPTER XXXIII

PULP AND PAPER INDUSTRIES

Cellulose is probably the most versatile raw material known to man, and its conversion to a group of products that are indispensible to modern civilization is the everyday function of the pulp and paper industry. This industry, which in 1937 employed over 150,000 persons in 841 pulp and paper mills and manufactured products valued at $1,205,132,000,[1] is a vital link in the chain of modern chemical factories, supplying not only purified cellulose for explosives and plastics but consuming large tonnages of sulfur, lime, chlorine, caustic soda, soda ash, starch, and many other chemicals.

Historical.—Man's earliest attempts to record human activities were made on stone. A little later, bark, leaves, and ivory were also used. Between 2500 and 2000 B.C. the manufacture of a writing paper from papyrus, a tall reed growing along the Nile, was begun. It is from this reed that the word *paper* is derived. There were, however, other early writing materials, including dried calf- and goatskin parchment, the wax-covered boards of the Romans, and the clay brick records of the Babylonians.

The actual manufacture of paper was invented by the Chinese about A.D. 150 but was kept secret until about 700, when the Arabs conquered Samarkand. By the end of the fourteenth century, the process of manufacture had undergone several improvements and was well known in southern Europe. The industry did not obtain a firm foothold in England until the seventeenth century, and it was almost the beginning of the eighteenth century (1690) before the first paper mill was established in America.

The only raw material used by the early industry was rags, which were washed, stamped into a pulp by water-driven stamping rods, and the resultant mass diluted. A wooden frame with a wire-screen bottom was dipped into the pulp and shaken as the liquor drained through, matting the fibers into a sheet. These sheets were placed on felts, stacked, pressed to remove additional water, and hung up to dry. The product was rag paper.

Between 1750 and 1800 the Holland beater was developed and adopted. In 1799, a Frenchman, Louis Robert, invented a process for forming a sheet on a moving wire screen. He disposed of his invention to M. Didot and John Gamble, who after making additional improvements sold out to the Fourdrinier brothers in 1804. This machine is known today as the *Fourdrinier* machine. In 1809 the cylinder machine was invented by John Dickinson and immediately forced the Fourdrinier into the background, where it remained until about 1830, when its importance was finally realized. It was in this period that the first Fourdrinier was received in America (1827) and that steam cylinders for drying were first used (1826).[1]

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[1] Opportunities in the Pulp and Paper Industry for Chemical Engineers, *Chem. & Met. Eng.*, **47**, 241 (1940).

TABLE 1 —WOOD CONSUMPTION IN PULP MANUFACTURE BY KIND[a]

Kind	Cords	Cost
Yellow pine, Southern	5,013,478	$ 27,557,380
Spruce	3,009,714	37,840,861
Hemlock	2,788,771	20,318,358
Poplar	598,675	5,532,099
Jack pine	477,975	4,310,939
Balsam fir	472,186	5,111,516
Beech, birch, maple	298,895	2,939,849
White fir.	213,445	1,568,522
Cottonwood	74,584	512,064
Tamarack (larch)	11,324	85,222
Other woods	509,976	3,059,404
Slabs and mill waste	274,935	903,744
Total	13,742,958	$109,739,958

[a] "Census of Forest Products 1940," U.S Department of Commerce, Bureau of the Census, Washington

The increased production made possible by the Fourdrinier and cylinder machines so greatly increased the demand for rags that a scarcity soon developed. In 1841, however, Keller of Saxony had invented a mechanical process of making pulp from wood. The soda process was developed by Watt and Burgess in the years 1853–1854. In 1866 and 1867 the American chemist, Tilghman, was granted the basic patents (British) for the sulfite process, although the commercialization of the process was carried out independently of Tilghman, by the Swedish chemist, C. D. Ekman, who began the manufacture of sulfite pulp at Bergvik, Sweden, in 1874. The sulfate or kraft process (*kraft* is German for strong) was the result of basic experiments conducted by C. F. Dahl in 1879, at Danzig. In 1908 the sulfate process was introduced into the United States. At that time, pulp production was divided as follows: mechanical, 48 per cent; sulfite, 40 per cent; soda, 12 per cent. Pulp manufacture gradually developed into an industry of its own and served industries other than the paper industry as well.[1]

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[1] JOHNSEN, The Pulp and Paper Industry, *Ind. Eng. Chem.*, **27**, 514 (1935).

The manufacture of pulp for rayon manufacture has assumed major importance and become a distinctly specialized division of pulp manufacture. Perhaps the greatest change in the industry in recent years has been the rise of the sulfate process to the position of major importance in the industry, a place held for years by the sulfite process.[2] This situation will undoubtedly continue.

The control and utilization of the industry's by-products have received widespread attention. The creation of useful materials from the lignin and the waste liquors means an increased income for the industry as well as a partial solution to its major problem, the avoidance of stream pollution.[3]

TABLE 2.—WOOD CONSUMPTION AND WOOD-PULP PRODUCTION BY PROCESS[a]

Process	Pulpwood consumption, cords	Wood-pulp production, short tons	Value
Mechanical	1,608,625	1,762,821	$ 32,753,955
Sulfite	4,965,908	2,591,684	128,983,210
Sulfate	5,975,334	3,725,135	102,578,341
Soda	979,360	548,047	27,939,508
Semichemical	213,731	164,940	2,735,127
Screenings, mechanical and chemical	....	59,113	533,938
Total	13,742,958	8,851,740	$295,524,079

[a] "Census of Forest Products: 1940," U.S. Department of Commerce, Bureau of the Census, Washington.

Uses and Economics.—Statistics for 1940 for the various types of wood pulp manufactured in the United States are given in Tables 1 and 2. Those for *paper* and *paperboard* manufactured in the United States in 1940 are presented in Table 3. The chief producing states were New York, Michigan, Wisconsin, Maine, Ohio, New Jersey, and Illinois, in the order named. They represented over 52 per cent of the country's total production, in which over 25 states were involved. Over half the world's production of paper is consumed in the United States.

MANUFACTURE OF PULP FOR PAPER

There are two distinct phases in the conversion of raw wood into the finished paper which is such an integral part of our everyday life. These are (1) the manufacture of pulp from the raw wood as outlined in Table 4 and (2) the conversion of the pulp to paper itself. Papermaking will be presented in a later section.

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[1] MURDOCK, Trends in Wood Pulp Industry, *Chem. & Met. Eng.*, **44**, 4 (1937).

[2] ANON., New Construction Is Changing the Industrial Complexion, *Chem. & Met. Eng.*, **44**, 652 (1937).

[3] ANON., Pulp and Paper, *Chem. & Met. Eng.*, **46**, 679 (1939).

TABLE 3.—PAPER AND PAPERBOARD PRODUCTION[a]

	Quantity, tons	Per cent of total
Newsprint	1,056,304	13.3
Ground-wood and specialty papers	550,453	6.9
Book paper, uncoated	1,655,423	20.6
Cover paper	26,944	0.3
Writing paper	599,452	7.4
Wrapping paper	2,500,818	31.3
Tissue paper, toilet, towel, etc.	761,712	9.6
Absorbent paper	129,410	1.6
Building paper	682,460	8.6
All other papers	60,120	0.7
Total paper	8,023,096	100.0
Container boards	3,434,834	53.2
Folding boxboard, bending	1,416,452	22.0
Setup boxboards, nonbending	898,549	13.9
Building boards	179,443	2.8
Bristol board	70,474	1.9
All other boards	449,796	6.2
Total paperboards	6,449,548	100.0

[a] "Census of Forest Products 1940," U.S. Department of Commerce, Bureau of the Census, Washington.

There are four different kinds of wood pulp: mechanical pulp, sulfite pulp, sulfate pulp, and soda pulp as shown in Tables 2 to 4. The first is prepared by purely mechanical means, the other three by chemical means. The mechanical pulp contains all of the wood except the bark and that lost during storage and transportation. Chemical pulps, however, are essentially pure cellulose, the unwanted and unstable lignin and the other noncellulosic components of the wood having been dissolved away by the treatment. Because of this, chemical pulps are much superior to mechanical (or ground-wood pulp) for fine papermaking. However, owing to the special processing required, they are too expensive for the cheaper grades of paper, such as newsprint.

Raw Materials.—Wood is the principal source of cellulose for papermaking (see Table 1). However, cotton, linen rags, and waste are also used by the mills, as well as the various hemps, their principal source being the cordage and rough waste of the textile industry.[1]

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[1] "The Manufacture of Pulp and Paper," Vol. III, 3d ed., sec. 1, p. 3, McGraw-Hill Book Company, Inc., New York, 1937. This is a three-volume detailed treatise on

All wood, whether consumed in the manufacture of the chemical pulps or of mechanical pulp, is subjected to a series of preliminary operations, including slashing and debarking. After arrival at the mill, the logs are conveyed by means of the log haul-up to the slasher. Here they are fed at an angle to a circular saw, 5 ft. in diameter and revolving at 750 r.p.m., which cuts them into blocks of convenient length, 24, 32, or 48 in. These blocks are conveyed to the barkers.

TABLE 4.—COMPARISON OF FOUR TYPES OF WOOD PULP

Type of process	Mechanical pulp	Sulfate pulp	Soda pulp	Sulfite pulp
Kind of wood	Soft, coniferous: spruce, balsam	Coniferous: southern pine, jack pine, spruce, balsam	Broadleaf woods: poplar, birch, maple	Coniferous: spruce most common
Fiber length, approximate	1½ mm.	2–3 mm.	1½ mm.	3 mm.
Principal reaction in digester	No digestion	Hydrolysis of lignins to alcohols and acids; some mercaptans formed	Hydrolysis of lignins to alcohols and acids	$RC{=}CR' + Ca(HSO_3)_2 \rightarrow RCH\text{-}CR'{\cdot}SO_3\frac{1}{2}Ca$
Composition of cooking liquor	No digestion	NaOH:40–65 g. per l. Na_2S:15–40 g. per l.	NaOH:11–13°Bé.	$Ca(HSO_3)_2$, 4.5 % total SO_2 and 3.1 % free SO_2
Digester, type and operation	No digestion; wood is ground to fiber on grinding stone under water	Unlined steel digester, pressure 125 lb., cooking time 3¼ hr.	Unlined steel digester, pressure 110 lb., cooking time 3–4 hr.	Cement, crushed quartz, and acid-resisting brick lining, pressure 70–160 lb., cooking time 10–11 hr.
Composition of spent liquor	No spent liquor	Total solids: 20 % Water: 80 %	Total solids: 16.4 %; water: 83.6 %; NaOH: 1.8 %	Spent liquor mostly wasted; SO_2 gas, evolved during cooking, recovered
Physical properties of pulp	Long, flexible, thin fibers. Deterioration occurs fairly rapidly	Long fibers, high strength, variable color	Short fibers, fair strength, very soft and opaque	Long fibers, fair strength, good color
Kinds of paper produced	Newsprint, wallpaper, wrapping paper, boxboard, wallboard	Kraft papers of all sorts, wrapping paper, bags, and container board; bleached now available	Books and magazines, some absorbent papers	Books, magazines, and rayon production

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the various phases of the pulp and paper industries, written by a number of experts under the direction of a committee of the paper industry of the United States and Canada.

There are two principal types of equipment used for debarking: barking drums and knife barkers. In the case of the drums, the wood is fed into the upper end of a rotating drum immersed in a tank partly filled with water where it is tumbled, the bark being literally rubbed off and the clean wood discharged at the other end. Full-sized logs are often charged to this type of equipment. Knife barkers, on the other hand, handle blocks only up to 2 ft. in length. The wood is placed horizontally against a rotating disk to which are fastened four to seven broad knives which continuously shave off the bark as the block is revolved.[1]

Mechanical Pulp.—This process involves no chemical treatment of the pulp whatsoever. The chief woods employed are spruce and balsam, which are of the soft, coniferous species. They have the advantage that they can be floated in streams to the mill, in contrast to poplar which sinks soon after immersion. After arrival at the mill, the wood is slashed and debarked. It is then ready to be ground, which is done in water to remove the heat of friction and to float the fibers away. The grinding is at an acute angle to the length of the blocks in order to furnish longer fibers by tearing rather than by right-angle cutting.

A widely used piece of equipment for grinding is the "three-pocket" type of grinder. This consists of a central grindstone mounted on a steel shaft and having three chambers or pockets around its periphery. The top of each chamber is surmounted by a hydraulic cylinder which operates a ram whose purpose is to force the blocks against the revolving stone. These stones are given a suitable type of burr by properly dressing their surface. Cooling and removal of the product are effected by means of a spray of "white water" which is returned to this point from a later step in the process. Another type of grinder that is sometimes employed is the magazine type which consists of a large, vertical, cylindrical chamber filled to the top with logs. The pressure of the wood on the grindstone at the bottom of the chamber is maintained by the weight of the wood in the magazine.

The pulp and water mixture from the grinders is dropped into a stock sewer below the grinders and is passed along to the sliver screen. Here the larger material is retained and discarded by the screen, while the fine material falls into the screened stock pit, from where it is pumped to the fine screens. The fines that pass these screens are concentrated in thickeners to give commercial mechanical pulp. The oversize from the fine screens is treated in refiners and then returned to the screens again. The water overflow from the thickeners contains about 15 to 20 per cent of the original fibers and is the so-called *white water* which is used in grinding and to aid flow in the stock sewer. As the process continues to operate, it is necessary to add fresh water to the system to keep down the temperature; therefore, some of the white water must be removed. Before being sent to waste, this water has the remaining fibers strained from it. The fiber is returned to the thickeners.[1]

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[1] *Ibid.*, sec. 2.

The *energy requirements* are all mechanical and consist chiefly of power for grinding. The only chemical change occurring in mechanical pulp is a slight hydration of the cellulose by long contact with water.

The *uses* of mechanical pulp are for the most part restricted to the cheaper grades of paper and board, where permanency is not required. The eventual deterioration that occurs in paper made from mechanical pulp is due to chemical decompositions of the noncellulosic portions of the wood. In the manufacture of newsprint, cheap manila, wall, tissue, and certain wrapping papers, the mechanical pulp is usually mixed with a small amount of chemical pulp.

Sulfate or Kraft Pulp.—This process is responsible for the major part of the pulp manufactured at the present time, as detailed in Table 2. Practically any kind of wood may be put through the process. However, coniferous woods are employed almost exclusively, since the process was developed especially to remove the large amounts of oil and resins in these woods. Yellow pine constitutes about 40 per cent of the wood used; tamarack, spruce, hemlock, balsam, jack pine, and white pine make up the remainder of the total.[2]

The *chemical reactions* are rather indefinite but involve hydrolysis of the lignins to alcohols and acids (see Table 4). This hydrolysis also produces mercaptans and sulfides, which are responsible for the familiar bad odor of sulfate pulp mills.

The *energy required* is given in Fig. 1 and largely involves mechanical energy to chip the wood and steam to heat up the chips in the digesters to the point where the noncellulosic material is rapidly dissolved.

The steps in the manufacture of sulfate pulp are depicted in the flow sheet of Fig. 1. These may be separated into the following sequences of *unit operations* (Op.) and *unit processes*[3] (Pr.):

The logs are slashed and debarked as previously described and conveyed to the chippers, which are large rotating disks holding four long heavy knives to reduce the wood to small chips (Op.).

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[1] *Ibid.*, sec. 3.

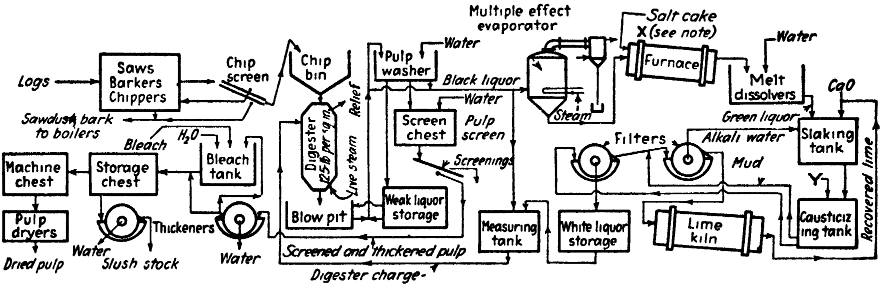
[2] *Ibid.*, sec. 4; STAMM and PETERING, Pulp from Wood, *Ind. Eng. Chem.*, **32,** 809 (1940).

[3] LEE, Paper Making at Savannah, *Chem. & Met. Eng.*, **44,** 356 (1937); LEE, West Virginia (Paper Co.) in South Carolina, *Chem. & Met. Eng.*, **44,** 432 (1937); GORDON and CREITZ, Elimination of Obnoxious Gases in the Sulfate Pulping Process, *Ind. Eng. Chem.*, **26,** 565 (1934); SKINNER, Bleached Sulfate Pulp, *Ind. Eng. Chem.*, **30,** 318 (1938); "The Manufacture of Pulp and Paper," Vol. III, sec. 5; *Chem. & Met. Eng.*, **46,** 727 (1939), pictured flow sheet.

The chips are screened on either rotary or vibrating screens to separate the oversized chips, the desired product, and the sawdust. The oversized chips and slivers are put through crushers or rechippers to reduce them to the proper size. They are then stored in a large chip bin from where they can be fed to the digesters by gravity (Op.).

The digesters are charged with chips, the cooking liquor containing essentially sodium sulfide and caustic soda is added, and live steam is turned on. Either a stationary or a rotary digester may be used. These are constructed of unlined steel. The pressure is raised slowly to 125 lb. per sq. in. The cooking period lasts about 3¼ hr. (Op. and Pr.).

At the end of this time the pressure is allowed to drop to 80 lb. and the charge is blown into the pit or into a battery of countercurrent diffusers, which are closed tanks designed to recover through heat exchangers the steam normally wasted in a blowpit; better washing also results.



Wood	2 4	tons	Per ton of dried sulfate pulp
New lime	325	lb	
Salt cake	450	lb	
Steam	10,000	lb	
Electricity	250	kw hr	
Direct labor	5	man hr	

Soda Process Note

With almost no variation this flow sheet may be taken for the soda process The principal change is in the omission of salt cake in the furnace at X where the sulfate is reduced to sulfide Make up soda ash is added in the causticizing tank at Y

Per ton of dried Pulp

Wood	1 5 2 tons	Steam	13 000 lb
New lime	500 lb	Electricity	250 kw hr
Soda ash	250 lb	Direct labor	5 man hr

FIG. 1.—Flow sheet for sulfate pulp and soda pulp.

The pulp after separation from the cooking liquor is washed (Op.).

The spent cooking liquor (black liquor) is pumped to storage to await recovery of its chemicals for reuse in the process (Op.).

The washed pulp is passed to the screen room where it enters the knotters which remove the knots that have failed to disintegrate in the cooking operation, then to screens that sieve out any small slivers of uncooked wood, and finally to filters and thickeners where a greater portion of the water is removed. The thickeners consist of cylindrical frames covered with fine wire screen rotating into the thin pulp. As it emerges, the water passes through the screen, leaving the pulp on the outside (Op.).

The removed knots are wasted, but the screenings are reduced in a refiner, prescreened, and returned to the diffuser chest (Op.).

The thickened pulp is next bleached. Two types of bleaching are employed: a one-stage process which consists of treatment with calcium hypochlorite bleach and produces a cream-colored paper, and a three-stage process which involves treatment with free chlorine, neutralization with milk of lime or caustic soda, and then a bleach with calcium hypochlorite. The bleaching agent in either case oxidizes and destroys the dyes formed from the tannins in the wood and accentuated by the sulfides present in the cooking liquor (Pr.).

After bleaching, the pulp should be washed and rethickened in preparation for making it into sheets dry enough to fold into a bundle called a *lap* (Op.); or it may be run into the charge chest of a paper machine to give dried pulp.

The lapping is done on a wet thickener which consists essentially of a cylinder dipping into a vat filled with stock solution, an endless felt belt which carries the pulp sheet through squeeze rolls, and a series of press rolls. The resulting laps contain 35 to 45 per cent air-dry fiber. These "wet" laps are stacked in hydraulic presses and subjected to pressures up to 3,000 lb. per sq. in. This product contains 50 to 60 per cent air-dry fiber (Op.).

Sulfate pulp, being made from coniferous woods, has the longest fibers of all the pulps. This, coupled with the fact that the chemicals used are not so harsh in their action as those employed for the other two chemical pulps, makes possible the production of very strong papers. In the past, the dark color of the kraft paper has limited its uses mainly to wrapping papers, sacks, and paperboard. However, newer developments in the bleaching treatment have made possible the manufacture of light-colored and even white pulps (see Fig. 2). This allows the mixing of this very high strength pulp with other types of pulp to increase the strength of the paper.[1]

Recovery[2] *of the Black Liquor.*—An important factor in the economic balance for the sulfate process has been the recovery of the spent liquor from the cooking process. The black liquor removed from the pulp in the pulp washer or diffuser contains 95 to 98 per cent of the total alkali charged to the digester. Most of the alkali is present as sodium carbonate or as organic compounds with sodium having properties very similar to the carbonate. Appreciable amounts of organic sulfur compounds are present in combination with sodium sulfide. There are also small amounts of sodium sulfate, salt, silica, and traces of lime, iron oxide, alumina, and potash. Total solids usually average about 20 per cent. This black liquor is first concentrated in multiple-effect or cascade evaporators to a concentration between 45 and 70 per cent total solids, depending on the type of recovery unit. This removal of water is necessary in order to produce a liquor that will ignite and burn when sprayed into the furnace.

Figure 3 shows a modern recovery system. Hot, concentrated liquor, to which has been added make-up sodium sulfate, is fed into the disk evaporator, countercurrent to the gas flow. As the charge moves down the furnace, water is evaporated and the organic salts are broken down. The resulting strong black liquor, containing almost all of the organic matter in the original black liquor, discharges into the smelting furnace.

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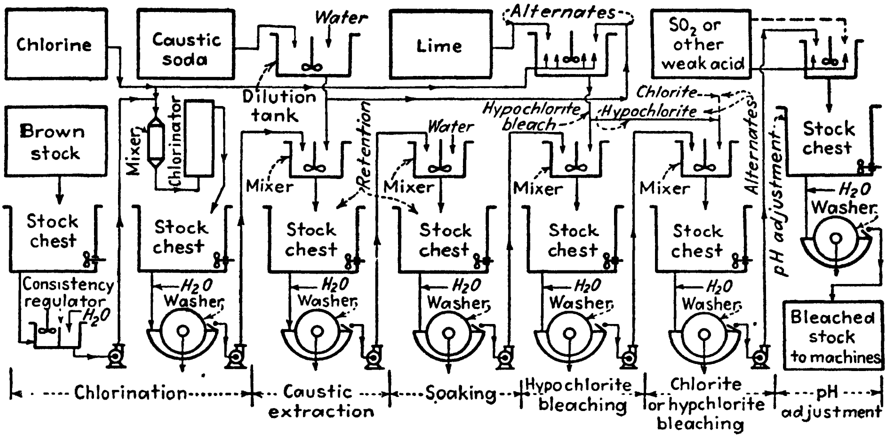
[1] "The Manufacture of Pulp and Paper," Vol. III, sec. 5.

[2] "Rogers' Manual of Industrial Chemistry," 6th ed., p. 1419, D. Van Nostrand Company, Inc., New York, 1942.



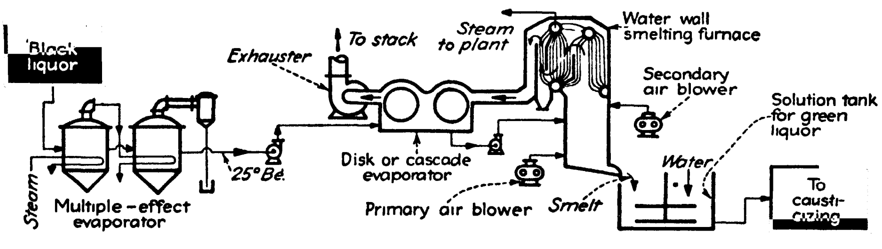
Chlorine (for pine)	160-200 lb.	Water	60,224 gal.	To bleach 1 ton dry sulfate pulp of 80-85 G.E. brightness
Chlorine (for hemlock)	140-180 lb.	Steam	3,120 lb.	
Caustic soda	40 lb.	Direct labor	2 men per shift	

FIG. 2.—Sulfate pulp bleaching—continuous sulfate or Kraft process.

Here any remaining organic compounds are broken down, the carbon is burned away, and the inorganic chemicals are melted. At the same time, the reaction

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2$$

takes place. The molten chemical "smelt" is allowed to fall into a weak



Recovery over 95 percent; 10,000 lb. steam produced per ton pulp

FIG. 3.—Black-liquor recovery. (*Courtesy of Combustion Engineering Company.*)

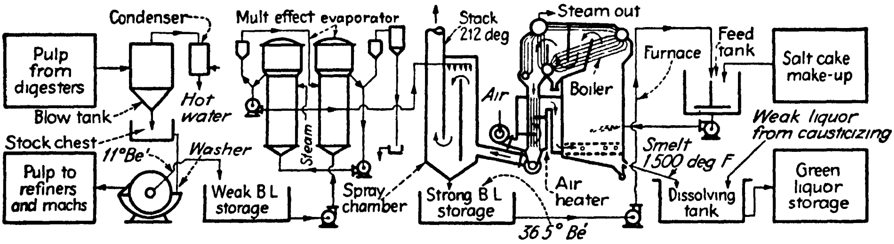
solution of "dissolving liquor" coming from the causticizing plant. The chemicals dissolve immediately to give a characteristic *green liquor*. The insoluble impurities are allowed to settle out and the liquor is then causticized by adding slaked lime prepared from the recovered $CaCO_3$.

The reaction

$$Na_2CO_3(aq) + Ca(OH)_2(s) \rightarrow 2NaOH(aq) + CaCO_3(s); \quad \Delta H = -2{,}100 \text{ cal.}$$

occurs quickly. The resulting slurry is separated by rotary continuous filters, using Monel metal screens as a filtering medium. The calcium carbonate sludge is sent to a limekiln to recover the CaO for reuse in the process. The filtrate is the *white liquor* used in the cooking of the fibers. It contains caustic soda, sodium sulfide, and small quantities of sodium carbonate, sodium sulfate, sodium sulfite, and thiosulfate.

Figure 4 shows another method of black liquor recovery. In this process the strong black liquor is sprayed into the furnace. The water is evaporated and the resulting material is heated to 1500°F. to remove organic compounds and melt the inorganic ones. The smelt is dissolved to form green liquor as described above.



Chemical recovery, 95 percent, Steam production, 10,000-12,000 lb per ton pulp

FIG. 4.—Flow sheet for black-liquor recovery from either sulfate or soda pulp—B. & W. Tomlinson process. (*Courtesy of The Babcock & Wilcox Company.*)

Among the by-products from the black liquor recovery plant is tall oil, a black, sticky, viscous liquid composed mainly of resin acids, fatty acids, and methanol.[1] The tall oil may be separated from the weak black liquor by means of centrifuges (in America), or obtained by flotation from the concentrated liquors (in Europe). It is used in the manufacture of soaps and greases and in the preparation of emulsions. Methanol may be recovered by dry distillation of the pulverized mass obtained by evaporation of the black liquor with barium hydrate. The cost does not permit economical recovery, however. The digester relief gases yield paying quantities of spruce turpentine, from 2 to 10 gal. per ton of pulp produced. This may be refined to produce sulfate turpentine.

Soda Pulp.—The manufacture of soda pulp is very similar to that of sulfate pulp, both being alkaline processes. The woods used are of the deciduous or broadleaf variety. Poplar makes up the largest tonnage and is also the easiest to cook. Other woods employed include birch, maple, chestnut, gum, and basswood. Owing to the tendency of broadleaf woods to sink, it is usually necessary to ship them by rail or truck to the mill rather than to float them in. The preparation of the wood for cooking is similar to that described above under Sulfate Pulp (see notes on Fig. 1). The cooking liquor has a density of 11 to 13°Bé. and contains 6 to 7 per cent caustic soda.

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[1] VILBRANDT, CHAPMAN, and CROCKIN, Sulfonation of Tall Oil, *Ind. Eng. Chem.*, **33**, 197 (1941); HASTINGS, Tall Oil, *Am. Dyestuff Reptr.*, **33**, 25 (1944).

The digesters are very similar to the digesters used in the sulfate process and are constructed of steel or wrought-iron plate, likewise unlined. The cooking time varies from 2 to 3 hr. at a pressure of 110 lb. per sq. in. and a temperature of 344°F. The digesters are usually blown to open blow pits instead of to diffusers, the steam being wasted. The pulp is washed in an open tank with a false bottom constructed of heavy steel plate covered with a fine wire netting. The plate is perforated with ½-in holes, closely spaced. The remaining operations are very similar to those used for processing sulfate pulp.

The black liquor from the soda pulp contains about 16 per cent total solids and 4.5 per cent total alkali. Most of the latter is sodium carbonate, the remainder being free sodium hydroxide. This liquor is concentrated by multiple-effect evaporation as in the sulfate process (Fig. 1) and fed to either stationary furnaces or rotary driers. No smelting furnace is used ordinarily, the product being a black ash (not fused) containing 20 to 25 per cent free carbon. This ash is charged to a series of leaching tanks equipped with false bottoms. The ash is leached countercurrently with water or weak alkali, the resulting solution being fed to the slaking tanks and the carbon waste discarded.

Recovered lime is added to the liquor in the slaking tank and the slurry fed to the causticizing tanks, where make-up sodium carbonate is added. The reaction taking place is essentially

$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3$$

The calcium carbonate sludge is filtered off and sent to the limekilns. The filtrate is the white liquor used in the digesters, all as outlined in Fig. 1.

Since the fibers from broadleaf woods are shorter (1½ mm.) than those from coniferous woods used in the sulfate process (2 to 3 mm.), the product of the soda process is a pulp that makes a weaker paper. Therefore, it is generally used with mixtures of other pulps, serving to fill in the spaces between the longer fibers. The largest tonnage of the pulp enters the manufacture of book, magazine, and tissue papers.[1]

Sulfite Pulp.—On the basis of quantity produced, this process ranks second only to the sulfate process. Although spruce is the wood most commonly employed, appreciable quantities of hemlock and balsam are also used. The wood is barked, cleaned, and chipped as described under Sulfate Pulp, the resulting chips being about ½ in. in length. It is then conveyed to the storage bins above the digesters, preparatory to being cooked.

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[1] "The Manufacture of Pulp and Paper," Vol. III, sec. 5.

The chemistry of the sulfite digestion of cellulosic materials is very complicated, and the thermodynamic data are incomplete and not very reliable. The external energy required for the process includes steam for the preparation of the cooking liquor and cooking the pulp, and mechanical energy for chipping the wood and pumping.

When wood is cooked with calcium bisulfite-magnesium bisulfite-sulfur dioxide liquor, the following reactions take place: The lignin is converted to calcium ligno-sulfonic acid by addition to the unsaturated portions of the lignin molecule. Some formic acid, acetic acid, and furfural are formed. Spruce turpentine, essentially *p*-cymene, is a product and appears in the relief gases. Approximately 14 lb. of methanol is produced per ton of pulp and is removed in the relief gases.

Two methods of preparing the cooking liquor (tower and milk of lime) and two methods of cooking (direct and indirect) are widely used. Figure 5 shows the preparation of sulfite pulp using the tower system and direct cooking. The essential reactions involved in the preparation of the cooking liquor are quite simple.

$$S + O_2 \rightarrow SO_2$$
$$2SO_2 + H_2O + CaCO_3 \rightarrow Ca(HSO_3)_2 + CO_2$$
$$2SO_2 + H_2O + MgCO_3 \rightarrow Mg(HSO_3)_2 + CO_2$$

The entire process may be divided into the following *unit operations* (Op.) and *unit processes*[1] (Pr.), as illustrated in Fig. 5.

Sulfur is melted in a tank heated by the rotary burner and then fed to this burner (Op.) for oxidation (Pr.).

Any sulfur that is vaporized in the burner enters a combustion chamber, where it is oxidized to sulfur dioxide. The amount of air in this operation is closely controlled to prevent the formation of sulfur trioxide (Pr.).

The sulfur dioxide obtained is cooled quickly in a horizontal, vertical, or pond cooler consisting essentially of a system of pipes surrounded by water. In all but the pond system the water is sprayed on the outside of the pipes (Op.).

The next step in the process is the absorption of the gas in water, in the presence of calcium and magnesium compounds. This is accomplished in a series of two or more absorption towers packed with limestone. A fine spray of water passes down through the tower system countercurrent to the sulfur dioxide gas, which is blown up through the tower (Op. and Pr.).

The liquor leaving the towers contains a certain amount of free sulfur dioxide, which is enhanced from time to time as the free sulfur dioxide vented from the digesters is bubbled through it in the "reclaiming tower" that follows. The final liquor as charged to the digesters is a solution of calcium and magnesium bisulfites, analyzing about 4.5 per cent "total" sulfur dioxide and about 3.5 per cent "free"[1] sulfur dioxide. The digester is filled with chips and the acid cooking liquor is pumped in at the bottom (Op.). The digesters are cylindrical steel vessels with a capacity of from 1 to 23 tons of fiber and 3,000 to 51,000 gal. of "acid." A special lining of cement, crushed quartz, and acid-resisting brick is used to avoid the corrosive action of the cooking liquor.

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[1] *Ibid.*, sec. 4; ANON., Sulfite Pulp, *Chem. & Met. Eng.*, **48**, No. 8, 106 (1941), pictured flow chart.

The digester is heated with direct steam. In recent years the industry has turned to digesters with forced outside circulation, which heat the cooking liquor in an outside stainless-steel tube heater and circulate it through the charge by means of pumps. This permits a better temperature distribution through the charge and prevents dilution of the liquor with the direct steam formerly used for heating. Conditions of the cook depend on the nature of the wood, the composition of the acid, and the quantity of pulp charged. The pressure varies from 70 to 160 lb. depending upon the construction of the plant. The time and the temperature range from 10 to 11 hr. and 105 to 155°C. (220 to 311°F.) (Pr.).

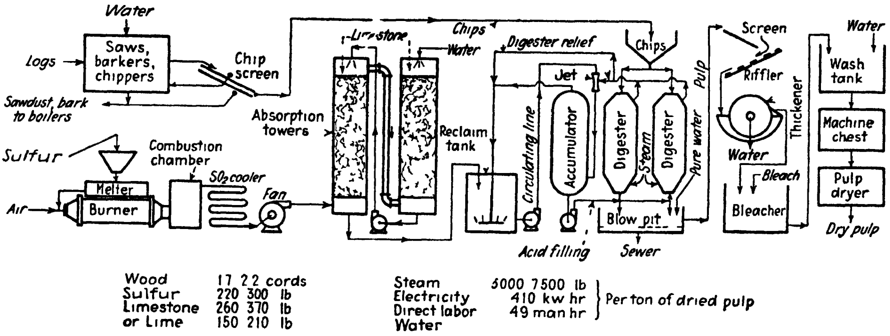

FIG. 5.—Flow sheet for sulfite pulp.

At the end of the cooking process the digester is discharged by blowing to a blow pit (a large, round tank having a false bottom and equipped with means to wash the pulp with fresh water). The cooking liquor is not recycled (Op.).

The pulp is pumped from the pit to a series of screens where knots and large lumps of fiber are removed (Op.).

The accepted stock from the screens is sent to the rifflers (a series of long felt-lined troughs equipped with cross bars every 6 ft.). The foreign matter in the pulp gradually settles out (Op.).

The relatively pure pulp is concentrated in thickeners which are cylindrical frames covered with 80-mesh bronze wire. The water passes through and the pulp is retained on the screen (Op.).

The pulp is sent to the bleacher, and free chlorine is introduced. After the chlorine has been exhausted, milk of lime is added to neutralize the mass (Pr.).

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[1] In the parlance of the pulp manufacturer, the "free" sulfur dioxide is the sum of that as sulfurous acid and that portion which requires alkali to convert from a bisulfite to a neutral sulfite.

The stock is washed (Op.), thickened (Op.), and sent to the machine chest.

Pulp from the chest is formed into laps of about 35 per cent dry fiber content (Op.), and the laps are dried with steam-heated rolls to a product which is 80 to 90 per cent dry fiber (Op.).

The milk-of-lime system of preparing the cooking liquor consists of slaking burnt lime containing a high percentage of magnesia with warm water to produce a 1°Bé. suspension. A high percentage of magnesia is desirable because the magnesium sulfites formed are more soluble than the corresponding calcium compounds. The calcium compounds tend to settle out and clog the pipes. This solution is treated with sulfur dioxide gas to produce the cooking liquor.

The indirect process of cooking utilizes a vertical or horizontal digester equipped with hard lead or copper steam coils. The cooking time is about 58 hr., and the maximum temperature and the pressure are 130°C. (266°F.) and 60 lb. per sq. in.

Sulfite pulp is a high-grade type of pulp and serves for the manufacture of some of the finest papers embracing the bond office line. It is used either alone or with some rag pulp to make writing paper and high-grade book paper.

Waste Sulfite Liquor.—Earlier in the description of the sulfite process it was mentioned that the lignin and other impurities in the wood were removed in the cooking step in the form of their calcium sulfonates. The disposition of a liquor containing most of the acid introduced into the process and almost 50 per cent of the weight of the original wood that went into the process presents quite a problem. Until very recently it was common practice to dump this liquor into a near-by stream, but legislation preventing stream pollution has practically stopped this.

Various means of utilizing the liquor have been proposed and used from time to time. Evaporated to fairly high concentration, it has been employed as a liquid fuel, a road binder, a core binder in foundries, and a binder for briquetting material. Other advocated uses include utilization as a tanning material, fertilizer, cattle food, and paper-sizing material. Recently a new process called the *Marathon-Howard process*[1] has been put into operation, which not only recovers the chemicals in the liquor but also reduces stream pollution. The process consists essentially in a three-stage lime-precipitation treatment which separates the waste liquor into (1) a calcium sulfite product for use in preparing fresh cooking acid, (2) an organic product which is essentially a basic calcium salt of lignin sulfonic acid, and (3) a process effluent having its biological oxygen demand reduced about 80 per cent in comparison with the original untreated liquor, and hence suitable for discharge to a stream.

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[1] ANON., Sulfite Liquor Development, *Chem. & Met. Eng.*, **46**, 618 (1939); SKINNER, Waste Problems in the Pulp and Paper Industry, *Ind. Eng. Chem.*, **31**, 1331 (1939).

The lignin precipitate may be pressed to yield a fuel suitable for burning, used as a raw material for vanillin production (over one third of the present United States vanillin is now produced from this source), as raw material for the manufacture of lignin plastic products, converted to magnesium and sodium salts, or used as the calcium salt in the tanning of leather, for treating boiler water, as a cement fixative, a dispersing agent, a grinding aid, etc.

Rag Pulp.—A small but important source of fiber for the manufacture of fine paper is rags. New rags are largely scraps from textile mills and garment factories, while the old rags are collected from the waste disposal from domestic sources. The rags go through a thrasher where dust is removed, before they can be sorted. All are separated according to color. Colors hard to bleach are used in the manufacture of dark papers, and the more easily bleached colors are employed for the lighter papers. After being sorted, the rags are cut into small squares, the dust is removed, and the squares are passed over magnets to remove metallic foreign materials. After this they are ready for the cook. In this operation the wax and resins in the fibers are removed, together with additional dirt and grease, and the dyes loosened from the fibers. The cooking liquors include either caustic lime, caustic soda, or a mixture of caustic lime and soda ash. The digester is a cylindrical, horizontal, rotary boiler holding about 5 tons of cloth. Cooking is continued for 10 to 12 hr. at 120°C. The resulting pulp is washed, bleached with chlorine and/or chloride of lime, and rewashed. It is then ready for manufacture into fine writing paper.

MANUFACTURE OF PAPER

The various pulps, even though frequently manufactured in coarse sheets, still lack those properties which are so desirable in a finished paper, such as proper surface, opacity, strength, and feel. Pulp stock is prepared for formation into paper by two general processes: beating and refining.[1] There is no sharp distinction between these two operations. Mills use either one or the other alone, or both together.

The most generally used type of *beater* (also known as a *Hollander*, Fig. 6) consists of a wooden or metal tank having rounded ends and a partition part way down the middle, thus giving a channel around which the pulp circulates continuously. On one side is a roll, equipped with knives or bars, and directly below this a bedplate consisting of stationary bars. In operation, the circulating pulp is forced between the bars on the revolving roll and the stationary bars of the bedplate. The roll itself may be raised or lowered to achieve the results desired. Beating the fibers makes the paper stronger, more uniform, more dense, more opaque, and less porous. It is in the beater that fillers, coloring agents, and sizing are added. Since the beaters are batch machines, some mills making lower grades of papers have done away with them entirely and use only refiners. The standard practice in making the finer grades of paper, however, is to follow the beaters with the refiners, which are continuous machines.

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[1] "The Manufacture of Pulp and Paper," Vol. IV, sec. 3; RICHTER, Wood Pulp Purification, *Ind. Eng. Chem.*, **33**, 1518 (1941); LEWIS, SQUIRES, and BROUGHTON, "Industrial Chemistry of Colloidal and Amorphous Materials," Chap. XV, particularly applicable to papermaking, The Macmillan Company, New York, 1942.

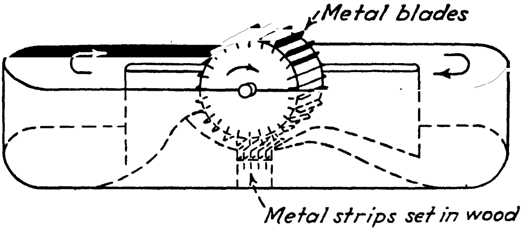

Fig. 6.—Hollander or beater.

The *Jordan* engine (Fig. 7) is the standard *refiner* and consists essentially of a conical shell, on the inside of which are set stationary bars. Revolving inside the shell is a core, also set with bars. It is the action between these two sets of bars that produces the desired effect on the pulp. The latter enters the small end of the cone and, after being acted upon by the bars, passes out at the other end.

Filler, *sizing*, and *coloring* may be added either in the beater, which is usual practice, in the Jordan, or in both. The order in which these materials are added to the beater may vary in different mills, but generally is as follows: (1) The various pulps are blended to give the desired density and uniformity. (2) The filler is added with or just after the fiber. (3) After sufficient beating the size is put in and mixed thoroughly. (4) The color is added and distributed well throughout the mass. (5) The alum is introduced to produce coagulation and the desired coating of fibers.

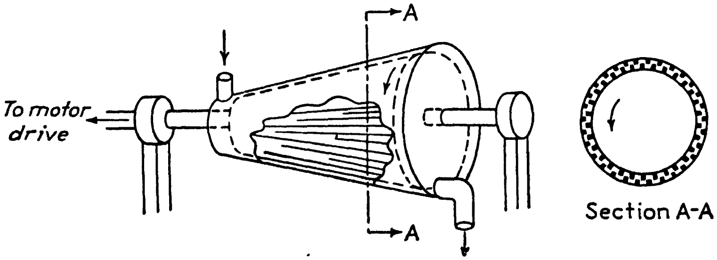

Fig. 7.—Conical refiner or Jordan engine.

All papers except absorbent types, *i.e.*, tissue or blotting paper, must have a filler[1] added to them, the purpose of which is to occupy the spaces between the fibers, thus giving a smoother surface, a more brilliant whiteness, increasing printability, and an improved opacity. The fillers are always inorganic substances and may be either naturally occurring materials, such as talc or certain clays, or manufactured products such as suitably precipitated calcium carbonate, blanc fixe, or titanium dioxide. All are finely ground.

Sizing[2] is added to paper to impart resistance to penetration by liquids. Again, the only papers not so treated are blotting and other absorbent papers, where penetration is desired. The sizing may either be added in the beating operation or applied to the surface after the sheet is formed. The process of engine sizing, *i.e.*, adding size in the beater, involves the addition of the sizing agent, consisting of either a soap made from the saponification of resin with alkali or a wax emulsion, followed by precipitation of the size itself with papermaker's alum, $Al_2(SO_4)_3 \cdot 18H_2O$. This treatment gives a gelatinous film on the fiber, which loses water of hydration and produces a hardened surface.

Tub sizing, on the other hand, is carried out on the dried paper, which may or may not have been previously and partly sized in the beating operation. The material used for this treatment must have adhesive properties, some of the more widely used substances being animal glue, gelatine, and starch. The operation is carried out either on the papermaking machine itself or in a separate sizing press employing air drying. The paper runs through a bath of the size material, then through rolls that remove the excess material, and finally over drying rolls. This type of sizing operation is used further to enhance the water resistance of the paper and especially to make it take ink evenly without blurring, even after erasures.

Another material that is added to the paper is *coloring*.[3] Approximately 98 per cent of all paper produced has a certain amount of coloring material added to it. Coloring, like sizing, may be added either in the beater or after the paper has been made, although about 95 per cent is added in the former manner. However, surface coloring, the latter method, uses less dye and requires the production of only one type of paper, which may be colored any shade later as needed.

All types of dyes (acid, basic, direct, sulfur) and all types of pigments (both natural and synthetic) are used as coloring agents. The acid dyes have no affinity for the cellulose fibers and must, therefore, be fixed to them by means of mordants. If the paper is colored in the beater, the alum that is added to precipitate the size will also act as a mordant for the dye.

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[1] "The Manufacture of Pulp and Paper," Vol. IV, sec. 4.

[2] *Ibid.*, sec. 5.

[3] *Ibid.*, sec. 6.

Surface dyeing may be carried out either in the papermaking machine or in a separate piece of equipment. In either case, the process consists in passing the paper through the dye bath, removing the excess dye by means of press rolls, and drying.

The machines used for the actual formation of the sheet are of two general types: the *Fourdrinier machine* and the *cylinder machine.* In 1938, there were 885 Fourdrinier machines operating in this country with a total daily capacity of 29,616 tons, and 690 cylinder machines with a total capacity of 22,614 tons.[1] The basic principles of operation are essentially the same for both machines. The sheet is formed on a traveling wire or a cylinder, dewatered under rollers, dried by heated rolls, and finished by calender rolls.

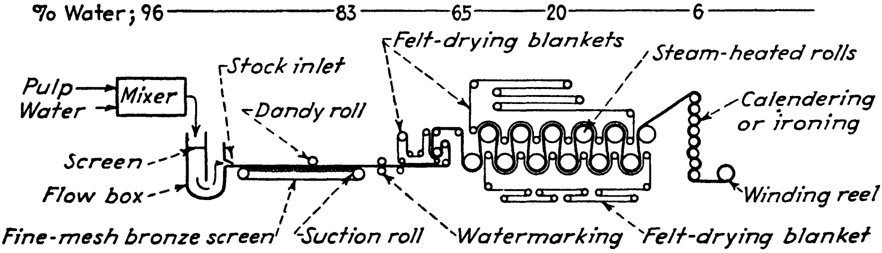

FIG. 8.—Fourdrinier machine.

Fourdrinier Machine.—Figure 8 shows the essential parts of a Fourdrinier machine. The stock from the foregoing operations, containing approximately ½ per cent fiber, is first sent through screens to the head box, from which it flows through the sluice onto a moving, endless, bronze-wire screen. The pulp fibers remain on the screen while a great portion of the water drains through. As the screen moves along, it has a sidewise shaking motion which serves to orient some of the fibers and give better felting action and more strength to the sheet. While still on the screen, the paper passes over suction boxes to remove water and under a dandy roll which smoothes the top of the sheet. Rubber deckle straps travel along the sides of the screen at the same speed and thus serve to form the edges of the paper.

From the wire, the paper is transferred to the first felt blanket which carries it through a series of press rolls, where more water is removed and the paper given a watermark if so desired. Leaving the first felt the paper passes through steel smoothing rolls and is picked up by the second felt which carries it through a series of drying rolls heated internally by steam. The paper enters the rolls with a moisture content of 60 to

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[1] ORR, The Modern Papermaking Machine, *Engineering*, **147**, 234 (1939).

70 per cent water and leaves them 90 to 94 per cent dry. Sizing may be sprayed on the sheet at this point, in which case it must pass through another series of drying rolls before entering the calender stack which is a series of smooth, heavy, steel rolls which impart the final surface to the paper. The resulting product, finished paper, is wound on the reel. The enormous quantity of water used makes it necessary to recirculate as much of it as possible for economical operation.

The operation of a Fourdrinier is a very complicated procedure. One of the major problems is making suitable allowance in the speed of the various rolls for the shrinkage of the paper as it dries. The operating speeds of the machines vary from 200 ft. per min. for the finer grades of paper, to 1,200 ft. per min. for newsprint.

Cylinder Machine.—For the manufacture of heavy paper, cardboard, or nonuniform paper, the cylinder machine is employed. It enables several similar or dissimilar layers to be united together into one heavy sheet. The cylinder machine has from four to seven parallel vats into each of which similar or dissimilar dilute paper stocks are charged. A wire-covered rotating cylinder dips into each vat. The paper stock is deposited on the turning screen as the water inside the cylinder is removed. As the cylinder revolves farther, the paper stock reaches the top where the wet layer comes into contact with and adheres to a moving felt. The traveling felt carrying the wet sheet underneath passes on under a couch roll to press out some of the water. This felt and paper come into contact with the top of the next cylinder and pick up another layer of wet paper. Thus a composite wet sheet or board is built up and passed through press rolls and on to the drying and smoothing rolls. Such a composite may have the outside layers of good stock while the inside ones may be of ground-wood pulp.

Paper Deinking.—For reworking waste paper to fine papers the ink must be removed. This is accomplished by a combination of various chemical and mechanical operations.[1] The old paper is sorted, shredded, dusted, and then cooked. The digester is either an open cooking tank with fume hood or a rotary boiler, live steam being used in either case. The cooking liquor usually employed is a weak caustic soda solution of about 8 per cent, the cooking time is around 10 hr.; the temperatures are in the neighborhood of 200°F. The purpose of the cooking process is to dissolve out the vehicle from the ink, thus breaking up the ink so that it may be removed. The cooked pulp goes to a series of screen washers similar to thickeners, where dirt and loosened carbon from the ink are removed. It may be necessary to put the pulp through a beater before washing, in order to aid in the loosening of the ink from the fibers. The washed pulp is bleached with either chlorine gas or chloride of lime, yielding in many cases a snow-white product. The recovered pulp is of such a quality that it is used in all fine grades of paper, mixed with new pulp in proportions that vary over a wide range.

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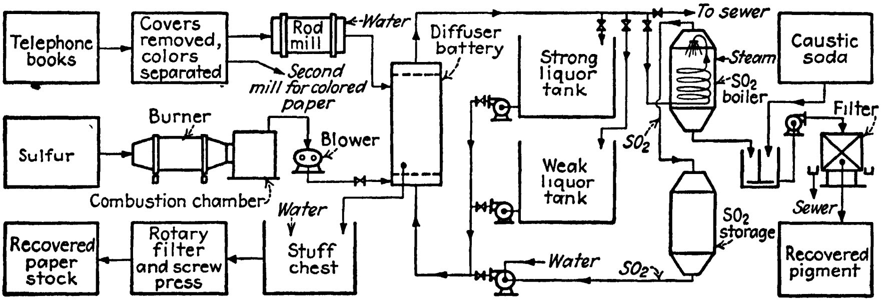
[1] Wells, De-inking and Reprocessing Paper Accomplished by New Methods, *Chem. & Met. Eng.*, **40**, 634 (1933).

Another method of deinking paper, which has found widespread favor particularly in the utilization of old telephone directories, is based on printing with an ink having an iron lake of hematin as pigment. Paper printed with this special ink is first disintegrated in rod mills and then treated with sulfur dioxide gas in diffusers. The sulfur dioxide serves to discharge the ink from the paper. The gas is added as such, as a strong liquor containing 6 g. of sulfur dioxide per liter, and then as a weak liquor containing 4 g. of sulfur dioxide per liter (see Fig. 9). The deinked pulp is discharged to a stuff chest and then to a rotary filter and screw press, finally yielding a recovered paper stock. The pigment is recovered from the spent liquor by neutralization with caustic soda and subsequent filtration in a plate-and-frame press. Part of the sulfur dioxide in the waste cooking liquor is recovered in a "SO_2 boiler," a waste containing 2 g. of sulfur dioxide per liter being discharged to the sewer.



Sulfur required: 40 lb. per ton pulp recovered

FIG. 9.—Flow sheet for paper deinking.

PAPERBOARD

The use of waste paper in the manufacture of pulp has reached a very important stage, the reasons being (1) the large supply available, (2) the small cost of making it into pulp, (3) the low original cost, and (4) the grade of product obtained. Over 5,000,000 tons of products from this waste are made yearly, as Table 3 shows. With only mechanical methods, old newspapers, wrapping paper, and boxboard may be made into pulp suitable for roofing paper and new boxboard. Since the product is dark colored, it is not necessary to remove the ink and pigments. Therefore, shredding and beating operations suffice.

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CHAPTER XXXIV

SYNTHETIC FIBERS

The ability of the chemist and the chemical engineer to create, from the test tube through the factory, products that are often superior to naturally occurring materials, is one of the outstanding accomplishments of this generation, and nowhere is it so graphically portrayed as by the modern synthetic fibers. Here is a group of synthetics which from their humble beginning in 1900 have grown to a total world production of more than 1 billion pounds in 1941. The United States started the manufacture of rayon in 1910 and produced in 1941 almost 600,000,000 lb., as shown by Fig. 1. These chemically made fibers competed with 200,000,000 lb. of silk, 600,000,000 lb. of wool, and 5 billion pounds of cotton. The list of synthetic fibers, which in 1900 included only nitro-cellulose, today has added to it a host of new products, including viscose rayon, acetate rayon, cuprammonium rayon, Cordura rayon, Aralac, Fiberglas, Teca, and the recently introduced Nylon and Vinyon. It is the purpose of this chapter to consider these synthetic fibers, their development, methods of manufacture, and uses, thereby presenting a picture of the chemistry and engineering behind our modern "fashions out of test tubes."

Rayon is manufactured as a uniform product in many varieties of size and texture. Because of this *uniformity* the textiles can be made more easily and, because of the *controlled variation*, more products are possible. Rayon is produced as a continuous or as a cut yarn, but uniform lengths of from 2 to 6 in. are known as *staple fiber*. The latter when twisted into yarn are known as *spun rayon* and possess a pleasing soft woolly feel. The rayon yarn results usually from twisting together a variable number of filaments ranging from 13 to 270 for most yarns. This is determined by the number of holes in the spinneret when the rayon is formed (see Fig. 4). Rayon is available with luster higher than that of silk and in delustered products so popular today. All these qualities have appealed to the consuming public and have caused what the Du Pont Company calls "growth through acceptance," leading to better and more attractive clothing.

Historical.—The idea of creating synthetic fibers is not new. In 1644, Robert Hooke prophesied that "silk equal to, if not better than that produced by the silkworm will be produced by mechanical means." However, it was not until 1855 that the first patent was issued for the preparation of artificial silk utilizing nitro-cellulose that had been discovered by Schönbein in 1845. Joseph Swan exhibited in London in 1885 fabrics woven from fibers prepared by squeezing collodion through fine orifices. It remained for Chardonnet to focus and utilize the work of all who preceded him and to establish the first commercial unit for producing artificial silk in 1891. Count Chardonnet has been called "father of the rayon industry."

The basic process of producing cuprammonium rayon was patented in 1890 and the viscose process was discovered in 1892. The first patent for the production of cellulose acetate filaments was issued in 1894.

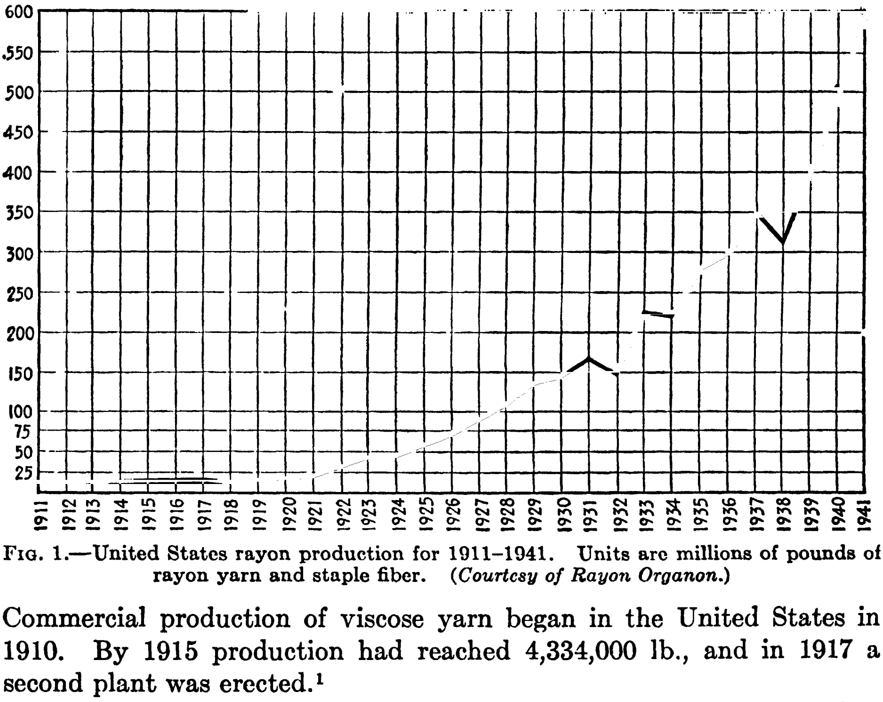

FIG. 1.—United States rayon production for 1911–1941. Units are millions of pounds of rayon yarn and staple fiber. (*Courtesy of Rayon Organon.*)

Commercial production of viscose yarn began in the United States in 1910. By 1915 production had reached 4,334,000 lb., and in 1917 a second plant was erected.[1]

The Tubize Chatillon Corporation began the United States manufacture of nitro-cellulose rayon in 1920. Cellulose acetate rayon was not made in America until 1924. By 1926 the production of the various types of rayon exceeded the consumption of silk, and by 1928 the United States consumption was 100,000,000 lb.

The viscose, cuprammonium, and acetate yarns proved superior to nitro-cellulose and, in 1934, the Tubize Chatillon Corporation closed its United States plant. Many new noncellulose fibers appeared, however, to more than take the place of nitro-cellulose rayon. Fiberglas, Nylon,

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[1] AVRAM, "The Rayon Industry," D. Van Nostrand Company, Inc., New York, 1927.

Vinyon, and Aralac have been placed on the market since 1934. Many others will probably appear soon. Protein fibers from soybeans[1] are in the pilot-plant stage and vinylidene fibers are being tested.

Uses and Economics.—Cotton has held the dominance of the textile fiber field for many years, but in the last decade it has been facing increased competition from synthetic fibers.[2] It is not so well known that cotton and cottonseed products are used in many industries in addition to the employment of cotton as a textile fiber. Of chief interest here are cotton linters as a raw material for the production of rayon.

In 1941, the United States production[3] and consumption of rayon filament yarn and staple fiber were as shown in Table 1 which indicates that viscose represents 60.8 per cent of the filament production, acetate 36.4 per cent, and cuprammonium 2.8 per cent. No cuprammonium rayon is used for the production of staple fiber; viscose dominates this field, 80.3 per cent of the staple fiber produced being viscose. The world's production of both filament and staple fiber is divided as follows: 80 per cent viscose, 15 per cent acetate, and 5 per cent cuprammonium. Consumption was apportioned approximately as shown in Table 2.

TABLE 1.—RAYON PRODUCTION AND CONSUMPTION

	Production, lb.	Consumption, lb.
Filament yarn:		
Viscose	274,459,000	
Acetate	163,745,000	
Cuprammonium	13,000,000	
Total	451,204,000	452,204,000
Staple fiber:		
Viscose	98,026,000	
Acetate	24,000,000	
Cuprammonium		
Total	122,026,000	133,626,000

TABLE 2.—PRODUCTS

	Percentage
Broad woven goods	66
Knit goods, other than hosiery	23
Hosiery	8
Narrow woven goods	2
Miscellaneous	1

The price of rayon varies according to the size of the filaments, process of manufacture, and type of finish, but it is around 50 cents a pound.

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[1] BOYER, Soybean Protein Fibers, *Ind. Eng. Chem.*, **32**, 1549 (1940).

[2] "A Plan and a Program," Cotton Research Foundation, Memphis, 1938.

[3] *Chem. & Met. Eng.*, **49**, No. 2, 97 (1942).

MANUFACTURE OF RAYON

Raw Materials.—The 1937 consumption of the main raw materials in the manufacture of rayon and its allied industry, the manufacture of cellulose film, was as shown in Table 3.

TABLE 3.—RAYON RAW MATERIALS

	Tons
Sulfuric acid, 50°Bé	380,000
Acetic acid, 100 per cent	24,000
Caustic soda, 76 per cent	186,000
Soda ash, 58 per cent	2,600
Sodium sulfates	8,000
Ammonia	500
Glucose	25,000
Cotton linters	14,000
Wood pulp	139,000
Carbon bisulfide	63,000

Up to a few years ago, the cuprammonium and acetate processes used only cotton linters as their source of cellulose, but recent trends even here are toward some sulfite pulp consumption. The viscose process has always been based on sulfite pulp. The preparation of the wood pulp has been described in Chap. XXXIII. Only pulp produced by the sulfite procedure is suitable. The cotton linters are obtained as follows: The seeds from the cotton gin, which have a considerable quantity of short fibers clinging to them, are cleaned to remove any foreign impurities such as leaves and sand and sent to the delintering machines. Here the short attached fibers, called *cotton linters,* are cut off by a row of disk saws. First and second cuts are made, the latter fibers being shorter but cleaner. They have the following typical analysis: cellulose (obtainable by caustic soda digestion), 80 to 85 per cent; ash, 1 to 1.5 per cent; iron, 0.06 per cent; ether extract, 1 per cent; lignin (insoluble in H_2SO_4), 3 per cent; moisture, 6 per cent. These linters are graded, examined, and tested by laboratory processing in the solution in which they are eventually to be used.

The purification and conversion to the so-called *chemical cotton* are accomplished as follows: A blend of raw linters is charged to a rotary digester, into which is pumped 3 per cent NaOH. Steam is introduced and the cotton cooked under about 60 lb. pressure for around 4 hr. The mass is dropped into a tank, washed, and bleached. The bleach tanks are preferably of stainless steel, with false, perforated bottoms; here calcium hypochlorite solution is added to the linters and the resulting discolored solution drained off. Sulfuric acid is used to accelerate the bleaching and reduce the ash content. Finally, the cotton is again washed. It is pumped over riffles to remove foreign matter and passed through rubber-covered squeeze rolls, which reduce the moisture content to about 50 per cent. The wet lumps are pulled apart in a "picker" and allowed to fall onto a conveyer which carries them through a tunnel drier and to the baler. The resulting product is chemical cotton, 98 per cent alpha cellulose (see Fig. 2 of Chap. XXII).

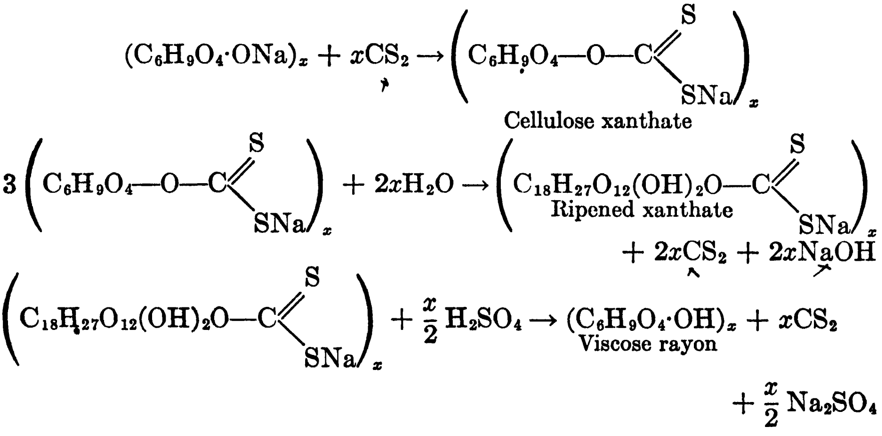
If sheet cellulose, the form used in viscose manufacture, is desired, the cotton, after the bleaching treatment has been completed, is blended with several other batches, passed successively through a beater and a refiner (see Manufacture of Paper in Chap. XXXIII) and formed into sheets on a Fourdrinier.[1]

The viscose process and the cuprammonium process produce a filament of regenerated cellulose, while the acetate forms a thread that is a definite chemical compound of cellulose, cellulose acetate. Although each of these processes is quite different as far as details of procedure are concerned, they all follow the same general outline: solution of the cellulose through a chemical reaction, aging or ripening of the solution (peculiar to viscose), filtration and removal of air, spinning of the fiber, combining the filaments into yarn, purifying the yarn (not necessary for acetate), and finishing (bleaching, washing, oiling, and drying).

REACTIONS

Viscose:[2]

$$\underset{\text{Cellulose}}{(C_6H_9O_4{\cdot}OH)_x} + x\mathrm{NaOH} \rightarrow \underset{\text{Alkali cellulose}}{(C_6H_9O_4{\cdot}ONa)_x} + xH_2O$$



$$(C_6H_9O_4{\cdot}ONa)_x + xCS_2 \rightarrow \underset{\text{Cellulose xanthate}}{\left(C_6H_9O_4{-}O{-}C\begin{smallmatrix}{\diagup\!\!\diagup}S\\ {\diagdown}SNa\end{smallmatrix}\right)_x}$$

$$3\left(C_6H_9O_4{-}O{-}C\begin{smallmatrix}{\diagup\!\!\diagup}S\\ {\diagdown}SNa\end{smallmatrix}\right)_x + 2xH_2O \rightarrow \left(\underset{\text{Ripened xanthate}}{C_{18}H_{27}O_{12}(OH)_2O{-}C}\begin{smallmatrix}{\diagup\!\!\diagup}S\\ {\diagdown}SNa\end{smallmatrix}\right)_x + 2xCS_2 + 2xNaOH$$

$$\left(C_{18}H_{27}O_{12}(OH)_2O{-}C\begin{smallmatrix}{\diagup\!\!\diagup}S\\ {\diagdown}SNa\end{smallmatrix}\right)_x + \frac{x}{2}H_2SO_4 \rightarrow \underset{\text{Viscose rayon}}{(C_6H_9O_4{\cdot}OH)_x} + xCS_2 + \frac{x}{2}Na_2SO_4$$

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[1] Munson, Manufacture of Chemical Cotton, *Ind. Eng. Chem.*, **22**, 467 (1930).

[2] The cellulose molecule is composed of a large undetermined number of glucose units, here represented as $(C_6H_9O_4OH)_x$. The value of x does not remain constant throughout these reactions. Each reaction causes a reduction in the molecular weight of the cellulose molecule, so that the viscose rayon molecule is considerably smaller than the original cellulose fed. Some CS_2 breaks away from the cellulose xanthate during the ripening process.

Cellulose Acetate:

$$\underset{\text{Cellulose}}{[C_6H_7O_2\cdot(OH)_3]_x} + 3x(CH_3CO)_2O \rightarrow \underset{\text{Cellulose acetate}}{[C_6H_7O_2(O_2CCH_3)_3]_x} + 3xCH_3CO_2H$$

Cuprammonium:

$$\underset{\text{Cellulose}}{(C_6H_{10}O_5)_x} + \underset{\text{Schweitzer's reagent}}{Cu(OH)_2 + NH_3} + H_2O \rightarrow \text{solution of cellulose}^1$$

$$\text{Cellulose solution} + \text{NaOH } (5\%) \rightarrow \text{partly coagulated cellulose}$$

$$\text{Partly coagulated cellulose} + H_2SO_4\ (1\tfrac{1}{2}\%) \rightarrow \underset{\text{Cuprammonium rayon}}{(C_6H_{10}O_5)_x}$$

The main energy requirements for any of these processes are for the mechanical operations of the pumps that force the solutions through the spinnerets and for the multitudinous other mechanical steps of the various processes. Little energy has to be supplied to cause the chemical reactions to occur.

VISCOSE MANUFACTURING PROCESS

From the standpoint of production volume, this is the most important of the three rayon processes, representing 65 per cent of all of the rayon manufactured in the United States. The finished filament is pure cellulose as shown by the equations but, because it consists of smaller molecules than the cellulose of the original wood pulp or cotton, it possesses different physical properties.

Unit Operations and Unit Processes.—The sequences of the process,[2] as shown in Fig. 2, can be broken down into the following *unit operations* (Op.) and *unit processes* (Pr.):

The raw materials (sheets made from wood pulp) are charged to a steeping press containing vertical perforated steel plates; the sheets of pulp and linters are steeped in a caustic soda solution (approximately 18 per cent) for 2 to 4 hr. at 56 to 62°F. (Pr.).

The excess liquor is drained off and recovered (Fig. 2). The soft sheets of alkali cellulose are reduced to small crumbs in a shredder (Op.). This requires 2 to 3 hr., and the temperature is maintained at 65 to 68°F.

The crumbs of alkali cellulose are aged for 48 to 72 hr. at 75°F. in steel cans. Some oxidation and degradation[3] occur, although the actual chemical change is unknown (Pr.).

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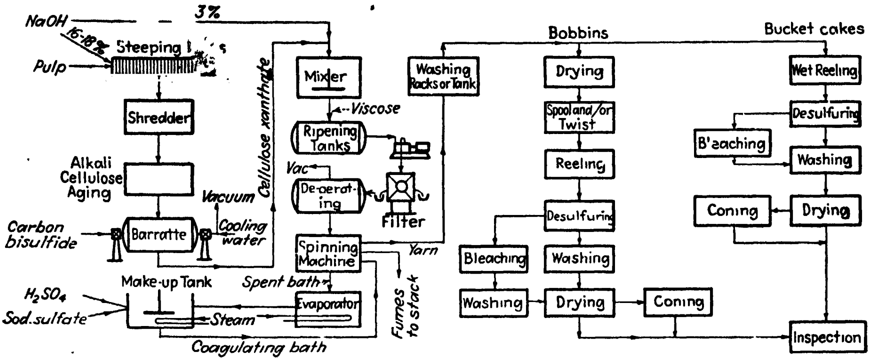
[1] This is a chemical reaction but the exact formula of the soluble reaction product is not known.

[2] ANON., Producing Cellophane and Viscose Rayon, *Chem. & Met. Eng.*, **46**, 25 (1939).

[3] LEWIS, SQUIRES and BROUGHTON, "Industrial Chemistry of Colloidal and Amorphous Materials," pp. 360*ff.* The Macmillan Company, New York, 1942.

After sufficient aging, the crumbs are charged into the barratte (a hexagonal, horizontal iron drum mixer with a hollow axis). Carbon disulfide in the ratio of 1 lb. of disulfide per 10 lb. of crumbs is added. The drum is rotated for about 3 hr., during which the crumbs gradually turn yellow and finally a deep orange and coagulate into small balls (Pr.).

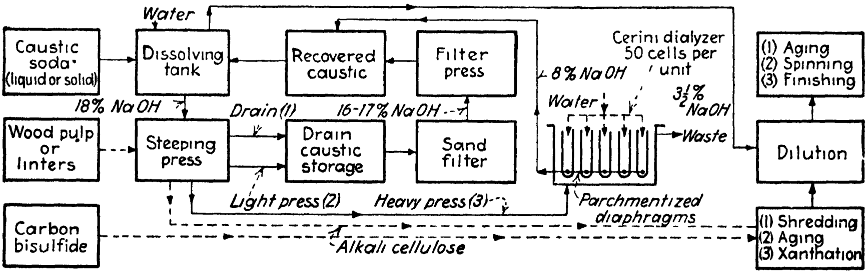


Wood pulp, linters	1.25 lb	Steam	70 lb.
Caustic soda, 76%	1 6 lb.	Refrigeration	002 ton
Carbon bisulfide	0.38 lb	Electricity	2-3 kw.-hr
Sulfuric acid, 60° Bé.	1.90 lb	Water	90-100 gal.

Direct labor, 0.5 man-hr.

Per pound of viscose yarn
Plant investment $1 ± 0.2 per lb. yr capacity

FIG. 2.—Flow sheet for viscose rayon.



New caustic soda	79 lb	Per 100 lb. pulp used
Recovered caustic soda	272 lb	
Water (based on solid caustic makeup)	910 lb.	

Caustic breakdown basis 100% NaOH	Use. Alkali cellulose	48 lb
	Dilution	27 lb.
	Recovery · Drain & press	228 lb
	Dialysis	44 lb.
	Loss:	4 lb

FIG. 3.—Flow sheet for caustic soda recovery in viscose manufacture—Cerini process.

The cellulose xanthate balls are dropped into a jacketed mixer (vissolver) containing dilute sodium hydroxide. The xanthate particles dissolve in the caustic and the final product, viscose solution, contains 61 per cent cellulose and 8 per cent sodium hydroxide (Pr.).[1] If desired, delustering agents such as titanium dioxide or organic pigments[2] are added to the viscose solution in the mixer.

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[1] AVRAM, *op. cit.*

[2] BENGER, Economic and Technical Aspects of the Rayon Industry, *Ind. Eng. Chem.*, **28,** 511 (1936).

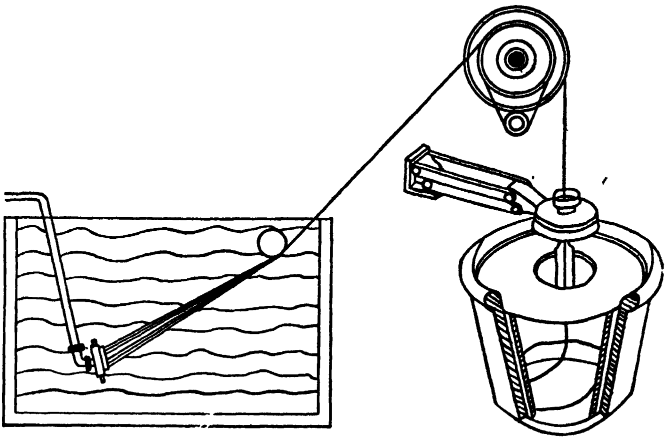

FIG. 4.—Spinning in viscose process. (*Courtesy of E. I. du Pont de Nemours & Company, Inc.*)

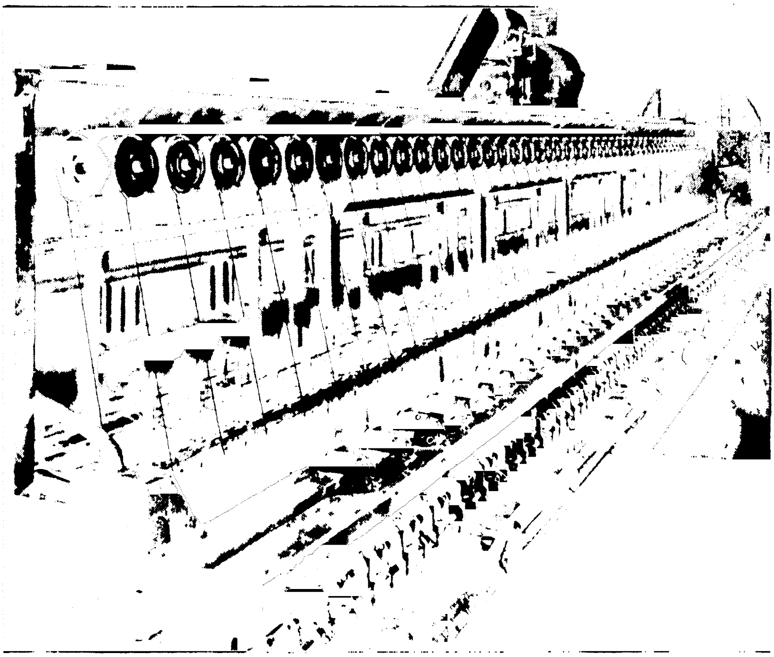

FIG. 5.—General view of bucket type of spinning machine at the Richmond, Va., plant of E. I. du Pont de Nemours & Company, Inc. The white lines up the face of the machine are the rayon threads as they leave the chemical baths. (*Courtesy of E. I. du Pont de Nemours & Company, Inc.*)

Several batches of viscose solution are blended and ripened for 4 to 5 days under rigidly controlled conditions at 66°F. and until the cellulose approaches nearly to the coagulating point. The percentage of combined sulfur decreases as some xanthic acid splits off and part of the cellulose is regenerated (Pr.).

At the end of this time the viscose solution is filtered through cotton batting (Op.) and placed under vacuum for 24 hr. to deaerate it completely since bubbles of air break the continuity of the filament (Op.).

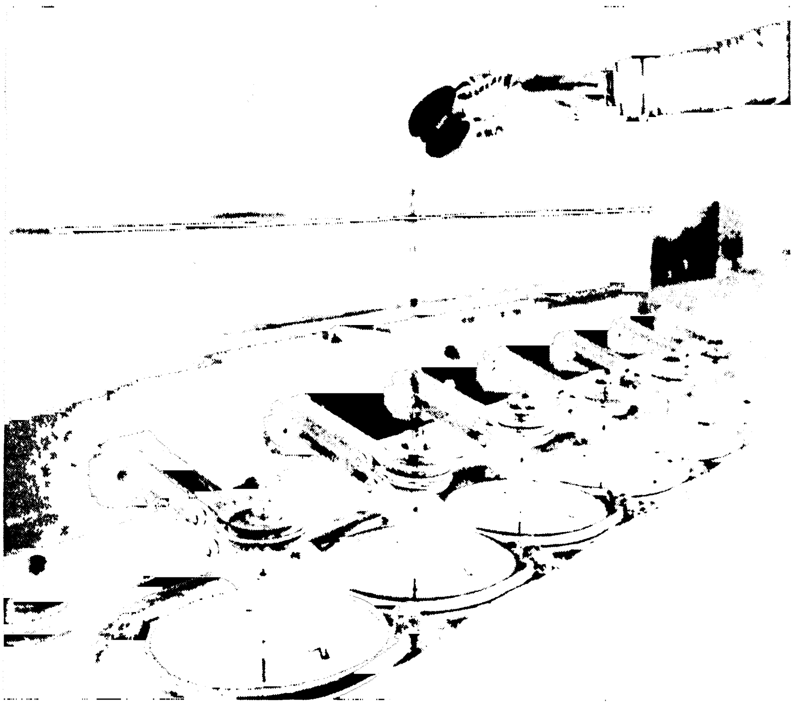

FIG 6.—"Threading up" a spinning machine Pulp used in the manufacture of rayon comes from the barrattes, it is treated chemically and becomes a reddish-brown sirup and is then fed through nozzles called spinnerets into an acid bath that hardens it again. A worker at a rayon plant of E I du Pont de Nemours & Company, Inc , near Richmond, Va., picks up the thin thread, passes it over a spinning machine, and guides it into buckets by a stream of water. (*Courtesy of E. I. du Pont de Nemours & Company, Inc*)

The solution is fed to the spinning machine. Two types are in general use: the bucket and the bobbin. Three-quarters of United States production uses the bucket type (see Figs. 4 to 6). The solution is extruded under pressure (gear pumps are used) through the spinneret into the spinning bath (Op.).

The spinnerets are small caps of noble metal, containing minute holes through which the solution is extruded, as depicted in Fig. 4. Just ahead of the spinneret are the candle filters to remove, in a final filtration, any foreign matter that might clog the holes. The spinning solution contains 8 to 10 per cent sulfuric acid to neutralize the caustic, 13.5 to 21.5 per cent sodium sulfate, about 1 per cent zinc sulfate to promote crenellation of the fiber, and 4 to 10 per cent glucose to prevent crystallization of the salts in the filaments. The solution from the spinnerets is coagulated in the bath as a filament of regenerated cellulose (Pr.).

If the bucket machine is used, the spinneret head dips horizontally into the spinning solution, several of the filaments are gathered into a thread and fed down to a small centrifugal bucket spinning at 7,500 r.p.m. (Op.). This is illustrated by Figs. 5 and 6. The bucket imparts one twist to the filaments per revolution and removes a greater portion of the occluded bath liquor through perforations in the periphery (Fig. 4).

If the bobbin machine is used, the spinnerets dip vertically upward into the spinning bath, and the filaments are wound on a revolving bobbin, as shown in Fig. 7 (Op.). No twist is imparted to the thread.

Yarn from either type is washed to remove the spinning liquor (Op.).

The bobbin yarn is dried (Op.), twisted, and skeined (Op.).

The bucket cakes are skeined without drying (Op.).

Both types of yarn are desulfurized by treating with a ¾ to 1 per cent sodium sulfide solution (Pr.).

Both types are washed (Op.), bleached in hypochlorite solution (Pr.), and washed again (Op.).

Both are dried (Op.) and coned (Op.).

Quite recently a continuous process[1] was put into operation, in which the entire treatment of the filament after extrusion, including washing, desulfurizing, bleaching, lubricating, drying, and twisting of the yarn is carried out continuously on one machine, without more than routine attention from the operators. The process reduces the entire series of operations, requiring by the old method as high as 90 hr., to about 6 min. and promises to revolutionize the entire industry.

It is possible to spin filaments of rayon that are hollow, by incorporating in the viscose solution sodium carbonate, which produces carbon dioxide in contact with the acid spinning bath. This yarn is later deflated. It is much more bulky per unit weight than solid filament viscose.[2]

Transparent viscose sheeting (Cellophane) is manufactured from a solution similar to that used for the rayon.[3] The spinning solution is extruded through a narrow slot into the coagulating bath. This may be done in a variety of ways, one of which is to cast the sheet onto a rotating drum, the lower end of which is submerged in the bath. The viscose film formed is transferred to succeeding tanks of warm water to remove the acid. It is desulfurized in a basic solution of sodium sulfide and rewashed. The characteristic yellow tinge must then be removed in a hypochlorite bleach bath, after which the sheet is rewashed. Then, in order to impart softness and pliability to the film, it is passed through a glycerine bath where it absorbs about 17 per cent glycerine, after which it is dried. Much of the Cellophane is subsequently made moistureproof by coating it on one side with a suitable lacquer of nitro-cellulose. The development of moistureproofing was due principally to W. H. Charch of the Du Pont Company, to whom has been awarded the 1932 Schoellkopf Medal of the Buffalo Section of the American Chemical Society for this achievement. Cellophane may be dyed, either with mordant dyes or direct colors. Owing to its attractive appearance as well as its moistureproofing, it is widely used as a packaging and wrapping material.

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[1] OLIVE, Viscose Rayon Spun Continuously, *Chem. & Met. Eng.*, **45**, 668 (1938); ANON., Continuous Production of Viscose Rayon, *Chem. & Met. Eng.*, **49**, No. 10, 116 (1942), pictured flow sheet.

[2] SHEARER, Rayon Manufacture with Particular Reference to Recent Technical Developments, *J. Soc. Chem. Ind.*, **55**, 468–472 (1936).

[3] HYDEN, Manufacture and Properties of Regenerated Cellulose Films, *Ind. Eng. Chem.*, **21**, 405 (1929); LEVEY, Films and Sheeting from Plastic Products, *Modern Plastics*, **14**, No. 8, 40 (1937); BRANDENBERGER, Notes on Cellophane, *J. Franklin Inst.*, **226**, 797 (1938); a pictured flow sheet for Cellophane is given in *Chem. & Met. Eng.*, **46**, 25 (1939).

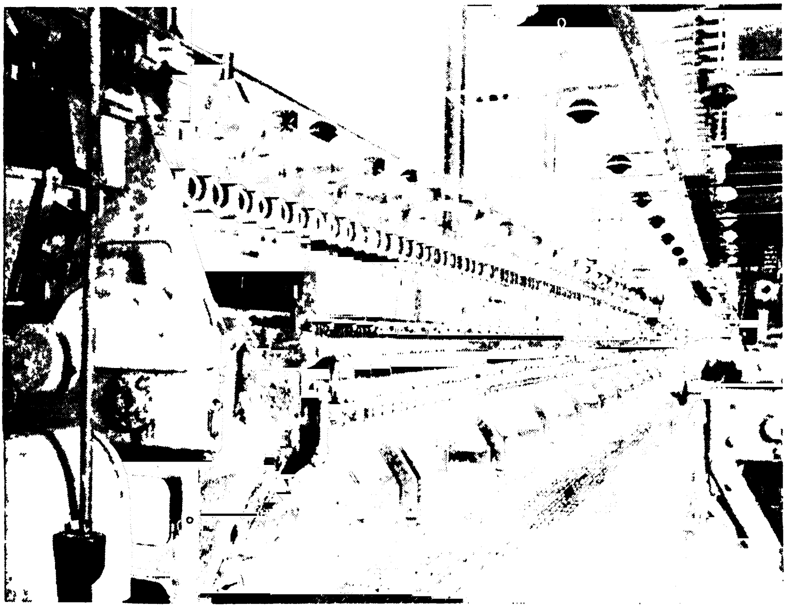


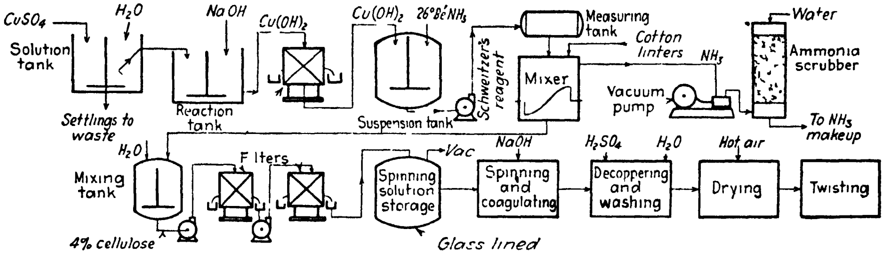
FIG. 7.—A spinning machine of the bobbin type used in the manufacture of rayon. (*Courtesy of E. I. du Pont de Nemours & Company, Inc.*)

Viscose may be used to prepare a durable cellulose sponge by placing a mixture of various sizes of Glauber's salt crystals, hemp or fibrous material, and viscose in a box, which is placed in the coagulating bath to regenerate the cellulose. The blocks are leached with warm water to remove the crystals of salt and cut into small-sized blocks for sale.

CUPRAMMONIUM MANUFACTURING PROCESS

Cuprammonium rayon is represented by the Furness process (Fig. 8), a continuous process that spins, coagulates, decoppers, washes, dries, twists, and spools the yarn in a total time of about 3 min. Bemberg cuprammonium rayon owes some of its desirable properties to "stretch" spinning, wherein the filaments are stretched during the coagulation in the spinning bath. This process can produce extremely fine yarns of as low as 15 denier and of great wet strength. The denier of a yarn is the weight in grams of 9,000 m. of yarn. Hence the finer the yarn, the smaller the denier.

Unit Operations and Unit Processes.—The spinning solution is prepared by charging 350 lb. of linters to a double-arm mixer with vacuum connections,



Cotton linters	0 92 lb	Sulfuric acid (60°Be)	0 8 lb est	Per pound of 11% moisture Rayon (Chem & Met estimates)
Ammonia (26°Be)	0 57 lb	Water	45 80 gal	
Copper sulfate (without recovery)	0 75 lb	Electricity	1 4 kw hr	
Caustic soda (50%)	0 80 lb est	Coal for steam	3 4 lb	
		Direct labor	0 2 0 5 man hr	

FIG. 8.—Flow sheet for cuprammonium rayon.

as shown in Fig. 8. The ammoniacal copper hydroxide solution (prepared by adding caustic soda to a copper sulfate solution, filtering, and dissolving the precipitate in a solution of 26°Bé. aqua ammonia) is run in and mixed (Op. and Pr.).

The excess ammonia is withdrawn through a vacuum line and the sirupy solution is diluted with water and filtered five times (Op.).

Aging of this solution is not necessary. The solution is forced vertically upward through a nickel spinneret into a coagulating bath of 5 per cent caustic soda (Op.).

The filament is coagulated (Pr.) and passed into a decoppering bath of 1½ per cent sulfuric acid (Pr.).

The yarn is washed (Op.), dried (Op.), and twisted (Op.) continuously by means of a specially designed cylindrical cage.[1]

Recovery of chemicals is very successfully accomplished; 95 per cent of the copper and 40 per cent of the ammonia are obtained again. The caustic soda is not consumed and is recycled.

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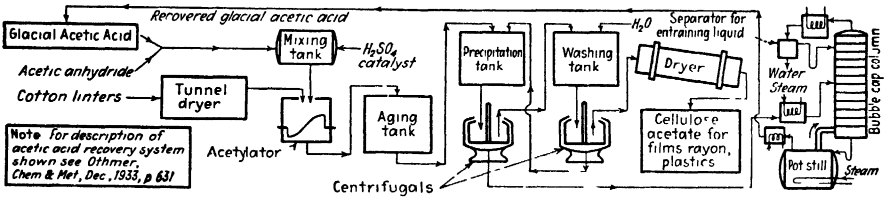
[1] CHASE, Furness Process Rayon, *Textile World*, **80**, 1888 (1931).

CELLULOSE ACETATE MANUFACTURING PROCESS

Cellulose acetate (or its homologs) is the only one of the rayons that is an ester of cellulose and not regenerated cellulose. The spinning solution may be used to produce rayons, transparent film, photographic film, the binder for safety glass, or precipitated to form molding powder for plastics and the basic constituent of cellulose lacquers.[1]

Unit Operations and Unit Processes.—The general sequence of operations (Fig. 9) is essentially the same as those of the other two rayon processes. The raw material for the spinning solution is prepared by charging 100 lb. of acetic anhydride, 100 lb. of glacial acetic acid, and a small quantity of sulfuric acid as a catalyst to a jacketed, glass-lined, agitated, cast-iron acetylator (Op.).

The mixture is cooled to 45°F. and 35 lb. of linters are added slowly. The acetylation requires 5 to 8 hr. and the temperature is maintained below 86°F. (Pr.).



Cotton linters	0.7 lb	Sulfuric acid	0.1 lb	Per pound of cellulose acetate
Acetic anhydride	2.0 lb	Direct labor	0.04 man hr	
Acetic acid*	3.25 lb	Acetone loss	0.3 lb	

* Recovery is about 5 lb per lb cellulose acetate

FIG. 9.—Flow sheet for cellulose acetate.

The viscous fluid is diluted with equal parts of concentrated acetic acid and 10 per cent sulfuric acid and allowed to age for 15 hr. at 100°F. Hydration of some of the acetate groups occurs (Pr.). No method has been devised at present whereby cellulose can be converted directly to a product of the desired acetyl content. It is necessary to transform it first to the triacetate and then partly hydrolyze off the required proportion of acetate groups.

The hydration is stopped by running the mixture into a large volume of water and precipitating the secondary acetate (Op.). The secondary acetate is centrifugated to separate it from the still strong acetic acid which is recovered, concentrated, and used over as shown in Fig. 9.

The flakes are washed several times by decantation (Op.) and then centrifuged to remove the remaining liquor (Op.). They are dried (Op.) and then are ready to be used in preparing the spinning solution.

The spinning solution is made by dissolving the dry flakes in acetone in a closed, agitated mixer and, if desired, the delustering pigment is added (Op.).

Several batches are blended, filtered, and sent to the spinning machine (Op.).

The solution is forced through the spinnerets into a current of warm moist air (Op.).

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[1] SMITH, Cellulose Acetate Rayons, *Ind. Eng. Chem.*, **32**, 1555 (1940).

The acetone evaporates and is recovered, leaving a filament of cellulose acetate (Op.).

These filaments are twisted and coned in the same manner as those of the previously described rayons (Op.).

The economical operation of the process depends on the recovery of as many of the chemicals as possible. Dilute acetic acid from various parts of the process is run through a Dorr thickener to remove last traces of acetate and then concentrated in one of the distilling units shown in Fig. 9 and described in Chap. XXXII. The acetone-laden air from the spinning machines may be passed through activated charcoal to adsorb the solvent (which is subsequently recovered by steaming and rectification) or by cooling the air in water towers and simultaneously dissolving out the acetone, the water-acetone mixture being subsequently rectified.

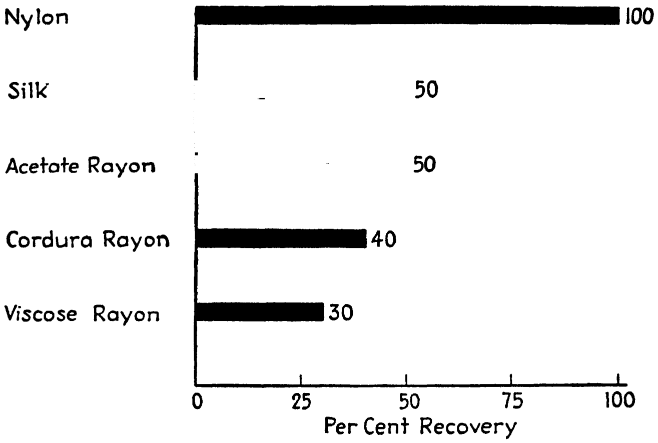

FIG. 10.—Textile fibers—elastic recovery after 4 per cent stretch. (*Courtesy of E. I. du Pont de Nemours & Company, Inc.*)

Quite recently the production of acetate staple has become of commercial importance.

The manufacture of transparent cellulose acetate sheeting comparable to Cellophane (viscose sheeting) is carried out by extruding an acetate dope of the required properties through a narrow slot onto a rotating drum where, in the presence of warm air, the acetone solvent evaporates. The resulting sheet is pliable and moistureproof. A trade-marked product is sold under the name Kodapak.

MISCELLANEOUS FIBERS

Glass Fibers.—Fiber glass was prepared for wearing apparel as early as 1893, when a dress of the fibers about five times the diameter of our present-day fiber was made by Michael J. Owens. Since that time, however, numerous improvements have been made, until at present fibers as small as 0.0002 in. in diameter and of indefinite length are possible.[1] This product known as *Fiberglas* is of great strength and of high corrosion resistance. It is employed woven around electrical wires and as a textile fiber. Recently Fiberglas has been very successfully used in combination with various plastics[2] in the construction of aircraft and accessories.

In order to use glass in textile fiber manufacture it is necessary to have a material equal in purity to the better grades of optical glass. Also, the molten glass must be free of any seeds or bubbles that would tend to break the continuity of the fiber. This is accomplished by first melting the glass in a large furnace and forming it into small spheres or marbles, which are rigidly inspected before being fed to the smaller textile furnace. The latter is equipped with a series of orifices constructed of platinum or some other noble metal. These orifices are electrically heated to permit more accurate control of the extrusion temperature and thereby permit reduction in the orifice opening and consequent smaller filaments. Below the furnace itself is a steam blower, which attenuates the stream of glass. This has replaced the old drum method formerly employed. The fibers from such a machine are 0.0002 in. in diameter. They are combined to make threads of the desired size by twisting. At the present time as many as 102 filaments are pulled at one time, at a rate of 6,000 ft. per min.

To manufacture glass wadding and glass wool, fairly short fibers are required. These may be produced by flowing a stream of glass onto a rapidly revolving refractory disk, which forms the threads and simultaneously throws them outward in both long and short lengths. The product is wadding. Still another method blows a stream of air under pressure around a vertical stream of glass flowing from an electrically heated platinum nozzle. This produces the now familiar glass wool.[3] Glass staple fiber is produced by flowing molten glass through a high-pressure steam jet.

Nylon.—Nylon[4] has been the sensation of the textile field because of its close approach to silk for hosiery and underwear and because of its unique elasticity and strength (see Figs. 10 and 11). It is being widely employed in the Second World War for parachutes, airplane-glider tow ropes, and silk replacements.

Although Nylon generally refers to all "synthetic fiber-forming polymeric amides having a proteinlike chemical structure," it is commercially the polymerized condensation product of adipic acid and hexamethylenediamine. These last-named intermediates are made from phenol, the adipic acid being prepared by hydrogenation to cyclohexanol and oxidation to the acid, and the diamine by amination of the acid with ammonia (*cf.* Chap. XXXIX and Fig. 12).

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[1] SLAYTER, Fiberglas, *Ind. Eng. Chem.*, **32,** 1568 (1940).

[2] ANON., Jettison Tanks for Ferry Service, *Modern Plastics*, **21,** No. 9, 75 (1944); KEMMER, *et. al.*, Glass-plastics, *Modern Plastics*, **21,** No. 9, 89–107 (1944).

[3] PLUMMER, Fiber-glass Mechanical Development, *Ind. Eng. Chem.*, **30,** 726–729 (1938).

[4] RAMSDELL, Nylon, *Am. Dyestuff Reptr.*, **33,** 121 (1944).

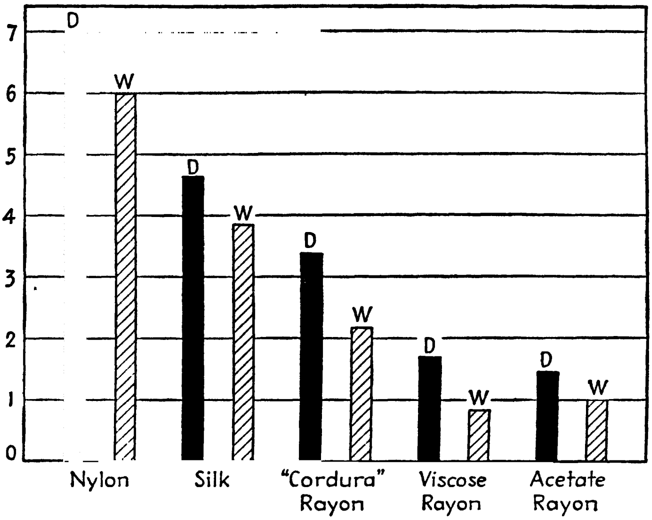
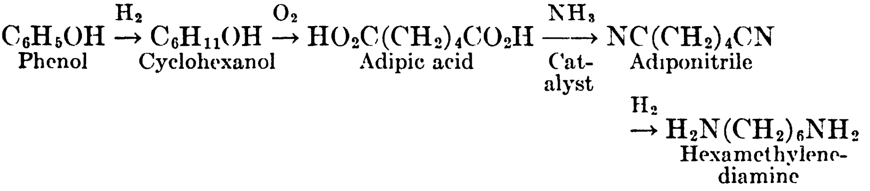


FIG. 11.—Textile fibers—tenacity in grams per denier. *D*, dry; *W*, wet. (*Courtesy of E. I. du Pont de Nemours & Company, Inc.*)

The reactions involved may be formulated as follows:



$$\underset{\text{Phenol}}{C_6H_5OH} \xrightarrow{H_2} \underset{\text{Cyclohexanol}}{C_6H_{11}OH} \xrightarrow{O_2} \underset{\text{Adipic acid}}{HO_2C(CH_2)_4CO_2H} \xrightarrow[\text{Catalyst}]{NH_3} \underset{\text{Adiponitrile}}{NC(CH_2)_4CN} \xrightarrow{H_2} \underset{\text{Hexamethylenediamine}}{H_2N(CH_2)_6NH_2}$$

$$xHO_2C(CH_2)_4CO_2H + xH_2N(CH_2)_6NH_2 \rightarrow -[OC(CH_2)_4CONH(CH_2)_6NH]_x - + 2xH_2O$$

The process[1] consists in heating the intermediates to a fairly high temperature under pressure to cause a combination of the adipic acid and the hexamethylenediamine as outlined in Fig. 12. The resulting Nylon salt is shipped, in solution, to the fiber plant, where its concentration is adjusted. It is polymerized in an autoclave to a long-chain linear polymer of a molecular weight of 10,000 or higher. The temperature is high enough to keep the polymer molten. The liquid material (melting point, 487°F.) is dropped onto a casting wheel chilled with cold water. A scraper removes the film of solid formed on the drum, and a chipper further disintegrates the polymer. These chips are dropped to small pressure chambers on the floor below, where they are remelted. The molten liquid is filtered and then extruded through spinnerets under nitrogen pressure into a stream of air, where they solidify immediately. The filaments are collected and wound on a bobbin. To impart the characteristic strength, the filaments are stretched by cold drawing.[1] This process "lines up" or orients the molecules so that they are parallel to the longitudinal axis of the fiber. The filaments are then coated, twisted, sized, and, in the case of hosiery yarn, baked. The resulting fiber is highly elastic, flammable, resistant to enzymes, mildew, mold, and moths. It is resistant to alkali but not to mineral acids, formic acid, and phenol. It is dyed readily with the usual dyes. Nylon possesses excellent physical properties, having a tensile strength greater than silk and a 100 per cent elastic recovery. In 1940, 35,000,000 pairs of women's stockings were made from Nylon, which increased to 109,000,000 pairs for 1941. In 1942, all Nylon fiber manufactured entered into war uses.

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[1] BERGEN, Nylon and Its Identification, *Rayon Textile Monthly*, **20,** 53 (1939); HOFF, Nylon As a Textile Fiber, *Ind. Eng. Chem.*, **32,** 1560 (1940); BOLTON, Development of Nylon, *Ind. Eng. Chem.*, **34,** 53 (1942); ANON., Du Pont Opens Nylon Plant at Martinsville, Va., *Chem. Industries*, **49,** 834 (1941), pictured flow sheet.

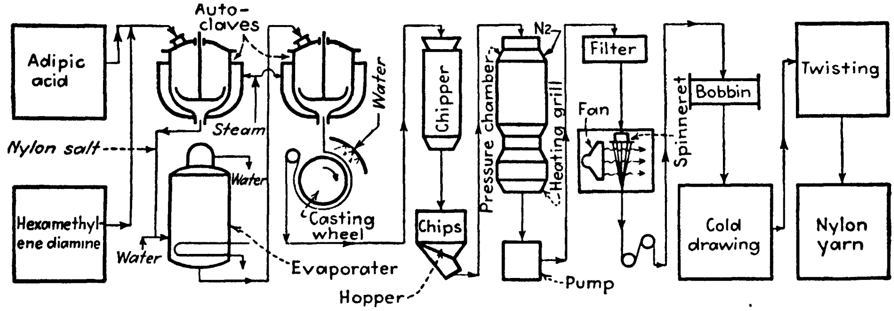

FIG. 12.—Flow chart for Nylon yarn.

Vinyon Fiber.[2]—Vinyon is a copolymer of vinyl chloride and vinyl acetate, the former being present in a concentration equal to 88 to 90 per cent of the mixture. It is thus a special form of the well-known vinyl resins. This polymer, which is a white, fluffy powder, is dissolved in acetone. The resulting dope, containing about 25 per cent plastic by weight, is filtered and deaerated much as described for cellulose acetate. The solution obtained is spun by the dry spinning process, being extruded into a current of warm air to remove the solvent. After standing for 12 hr. the filaments are twisted and stretched to about 1½ times their original length. This stretch is next "set" by soaking in water at 100°C. for 3 hr. It is ready to be coned for use. The fibers are not attacked by alkalies or mineral acid, alcohols, or aliphatic hydrocarbons but are thermoplastic above 65°C.

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[1] Boxer, Chemistry of Fibers Made by Carothers, *Am. Dyestuff Reptr.*, **31**, 16 (1942).

[2] Heymann, Vinyon Synthetic Fibers, *Am. Dyestuff Reptr.*, **30**, 575 (1941); Bonnet, Vinyon, *Ind. Eng. Chem.*, **32**, 1564 (1940); *Am. Dyestuff Reptr.*, **33**, 127 (1944).

Casein Fiber.—This is the so-called *artificial wool*, introduced in Italy as Lanital and made from casein (from milk) as a raw material. Either hydrochloric or lactic acids are used for the precipitation of the casein (*cf.* Chap. XXXIX). To make the fiber,[1] the casein is dissolved in an alkali bath, and the mixture so formed allowed to ripen to a paste of the required viscosity. This is then extruded through spinnerets into an acid-formaldehyde bath. The bath may also contain aluminum compounds for increasing the strength and water resistance of the fiber, and certain fats to add flexibility to the fiber. The filament is highly crease-resistant, possessing 25 to 35 per cent stretch. It resembles a damaged wool and accepts the standard wool dyes quite well. Its main disadvantages are its low tensile strength, both dry and wet, and its reaction to acid. Under the name *Aralac*, a similar product is now being manufactured in the United States by The National Dairy Products Corp. This may serve to utilize the casein obtainable from skim milk in a profitable manner. It is also an example of *chemurgy* or the blending of chemistry, industry, and the farm.

Vulcanized Fiber.—Cotton and linen rags form the basis of vulcanized fiber. The rags are treated to form paper, as described in Chap. XXXIII. The paper is gelatinized by a 70°Bé. solution of zinc chloride and is wound on a heated iron roll until the desired thickness is obtained. The fiber is washed thoroughly with gradually decreasing strengths of zinc chloride solution and finally with water to remove completely all zinc chloride. The fiber sheet is dried, flattened, and calendered by passing it through heavy rolls. This material is very tough and resistant to abrasion and is used for waste baskets, trunks, and other shipping boxes or containers.

FINISHING AGENTS

Finishing agents play a very important part in the production of merchandisable fabrics. They are used to improve the draping qualities, wearability, resilience, tensile strength, and drying properties. The finishing agents used are very numerous and depend upon the fiber to be treated and the particular final property desired. They may be polar compounds of fatty acids, either anionic or cationic, or they may be synthetic resins. The method of application varies with the agent used and the fiber, but they are usually applied in a dilute water solution to yield maximum penetration of the fiber.[1]

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[1] Borghetty, In Defense of Lanital, *Am. Dyestuff Reptr.*, **27**, 156 (1938); Bergen, Casein Wool, *Am. Dyestuff Reptr.*, **25**, 146 (1936); Whittier and Gould, Making Casein Fiber, *Ind. Eng. Chem.*, **32**, 906 (1940); Atwood, Products from Casein, *Chem. Industries*, **51**, 864 (1942); Prisley, Aralac, *Am. Dyestuff Reptr.*, **32**, 532 (1943).

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[1] ACKLEY, Cationic Finishing Agents, *Am. Dyestuff Reptr.*, **30**, 461 (1941); POWERS, Resins and Plastics for the Modification of Textile Fabrics, *Ind. Eng. Chem.*, **32**, 1543 (1940).

CHAPTER XXXV

PLASTICS

The development of plastics from laboratory curiosities to recognized products of industry has brought new and economical materials of construction to the engineer and the designer. Not only may plastics partly replace metals and other materials but they may also be used with them. The common basic raw materials are coal, petroleum, cotton, wood, gas, air, salt, and water. Plastics lend themselves to exceedingly wide application because of their *toughness, water resistance, ease of fabrication, and remarkable color range.* In this chapter the term *plastics* refers to the rigid materials that in their course of manufacture have been *plastic* in some stage but when used are *rigid,* showing no or only a moderate deformation under usage. This excludes the related products known as *rubbers* or *elastomers.*

Plastics and resins may be defined as organic materials that can be easily molded or shaped by mechanical or chemical action to give tough, noncrystalline substances[1] that are solid at ordinary temperatures. These solids may have various substances incorporated with them to impart color and strength. They are resistant to the action of many chemicals and atmospheric conditions.

The use of a plastic material for any specific application is dependent upon its composition, its particular properties, and the design of the part. Synthetic resins are the largest source of plastics with cellulose derivatives ranking next. The great utility of plastics may be shown by reference to a few typical applications in the various fields where these new materials are being applied. In the automotive and airplane industries many different plastics find specific utilization because of beauty, strength, oil and electrical resistance. Their resiliency and strength make them very useful in the manufacture of safety glass, laminated gears, cams, pulleys, self-lubricating bearings, plywood, and the like. In other fields where the plastic cannot be used itself, it is employed in combination with metals, as in the manufacture of steering wheels and plastic-covered dashboards. These combinations develop the best properties of each material.

In the electrical industries, molded and laminated organic plastics are of real value as solid insulating materials because of their good electrical properties and relatively high mechanical strength. The phenolic resins are used in most of the parts operating under ordinary voltage conditions. For very high frequencies and severe voltage gradients, polystyrene has more desirable characteristics and rivals the best inorganic insulators now available. The civil engineer's investigation of stress analysis has been greatly improved by the aid of transparent plastics that show distortion under stress. By building structural models out of fabricated plastics and by using movie film (plain or color), the effects of applied stress and strain can be studied advantageously for the improvement of structural design. Recently organic plastics have entered into competition with the older materials for construction in the chemical process industries. Such plastic materials[1] are inherently resistant to corrosive gases, liquids, and chemicals, and they are being used in the form of tubing and piping, plain or laminated piping,[2] tanks, absorption towers, etc.

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[1] LEWIS, SQUIRES, and BROUGHTON, "Industrial Chemistry of Colloidal and Amorphous Materials," pp. 140–147, The Macmillan Company, New York, 1942.

In the field of the decorative arts plastics have unlimited scope. They have been used to "dress up" all types of articles by eliminating harsh contours and by imparting almost any color combination conceivable. Only in the laminated phenolic resins is the color range limited.

Classification.—Plastics may be classified in various ways. On the basis of raw materials they may be simply grouped as synthetic resins, cellulose derivative plastics, natural resins, and protein products.[3] A raw-material classification[4] shows two main groups of synthetic resins: (1) those derived from coal tar and (2) those utilizing products of noncoal-tar origin. Group (2) may be further subdivided into (*a*) plastics based on cellulose and plant products, (*b*) those derived primarily from the hydrocarbons of petroleum, natural gas, and acetylene, (*c*) the urea resins, and (*d*) those derived from rubber and alkyl chlorides.

Plastics and resins can best be arranged according to their broad general application into thermosetting, thermoplastic, oil-soluble, and protein products, as presented in Table 1. This arrangement parallels chemical behavior. Plastics and resins may be formed as a result of (1) condensation or polymerization reactions, (2) plasticization of cellulose esters and ethers, and (3) interaction of protein materials with formaldehyde. In general, the synthetic resins of the thermoplastic type are formed by polymerization, and the synthetic resins of the thermosetting type are formed by condensation and polymerization. Proper reaction conditions of time, temperature, catalysts, and concentration of reactants influence the molecular weight which directly affects the physical properties of the resin. The cellulose derivatives are thermoplastic materials because of the inherent properties of the long-chain molecular structure of cellulose.

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[1] TARR, Plastics in Chemical Industry, *Ind. Eng. Chem.*, **27**, 1284 (1935); KLINE, RINKER, and MEINDL, Resistance of Plastics to Chemical Reagents, *Modern Plastics*, **18**, No. 4, 59 (1941).

[2] PIERCE, Extruded Tubing in War Production, *Modern Plastics*, **19**, No. 12, 55 (1942); PERRY, *op. cit.*, pp. 916–919; ENZ, Laminated Plastic Pipe for Chemicals, *Modern Plastics*, **19**, No. 12, 58 (1942).

[3] KLINE, "Organic Plastics," *Nat. Bur. Standards Circ.* C-411 (1936).

[4] ESSELEN and BACON, Raw Materials of the Plastics Industry, *Ind. Eng. Chem.*, **30**, 125 (1938).

The *thermosetting resins* are obtained from fusible intermediates which, under the influence of heat, pressure, and a catalyst, undergo chemical changes of condensation and polymerization to form a rigid final shape which is unaffected by heat or solvents. The molded articles, after setting and curing in the molds, may be removed hot without warping. The degree of resistance to heat and solvents may be modified by the addition of materials that cause structural changes. The thermosetting resins owe their heat-resisting properties to a *cross-linked structure*—a three-dimensional molecule.

TABLE 1.—CLASSIFICATION AND TYPES OF SYNTHETIC RESINS AND PLASTICS

1. Thermosetting resins (condensation and polymerization):
    - Phenolics or phenol(cresol)-aldehyde resins, as Bakelite, Durez, Resinox, Haveg, Catalin, Formica, Indur
    - Amino-aldehyde or urea-formaldehyde resins, as Plaskon, Beetle
    - Alkyd or glycerine-phthalate resins, as Glyptal, Rezyl, Beckosol, Dulux
2. Thermoplastic resins (including cellulose derivatives):
    - Cellulose derivatives:
        - Cellulose nitrate with camphor, as Celluloid, Viscoloid
        - Cellulose acetates, as Lumarith, Kodapak, Tenite, Plastacele
        - Cellulose acetate-propionates, as Hercose AP
        - Cellulose acetate-butyrates, as Hercose C
        - Ethyl cellulose, as Sylvanic, Ethocel
        - Benzyl cellulose
    - Polymer resins (polymerization):
        - Acrylate or polyacrylates, as Plexiglas, Lucite, Acryloid
        - Vinyls or polyvinyl resins, as Vinylite, Gelva, Butacite, Koroseal, Alvar
        - Polyvinylidine resin, as Saran
        - Styrenes or polystyrene resins, as Styron, Lustron
        - Coumarone and indene resins, as Cumar, Nevindene
        - Polyamides, as Nylon (condensation and polymerization).
3. Oil-soluble or modified resins:
    - Modified alkyds, as oil-soluble Rezyl
    - Modified phenolics, as Albersols, Amberol, Lewisol
    - Ester gum (rosin ester of glycerine)
4. Protein substances:
    - Casein-formaldehyde, as Galalith, Ameroid, Galorn
    - Zein (corn protein)-formaldehyde
    - Soybean protein-formaldehyde

The *thermoplastic resins* frequently are obtained from substituted derivatives of ethylene which can be made to polymerize under the influence of heat and catalysts. These materials are softened by heat and affected by certain solvents. When molded, they must be cooled in the mold before discharging so that no warping occurs. A notable feature of these resins is the ability of their scrap or rejects to be reworked along with new material. The structure of the thermoplastic resins is that of a *linear* or *string molecule.* Under thermoplastic materials should be included the cellulose derivatives, chiefly plasticized esters and ethers. These compositions, like the synthetic thermoplastic resins, are softened by heat. However, the degree of softening can be controlled by the amount of plasticizer added. The scrap can be reworked also.

Another class of resins becoming more important each year are the modified or *oil-soluble resins.* These are frequently placed as a subclass under thermoplastic resins. Normally, the phenol-formaldehyde type of resins or glyceryl-phthalate resins are not soluble or dispersible in fatty oils to make suitable protective surface coatings. If, during the processing operations, a para-substituted phenol is incorporated with the phenol and formaldehyde, then the normal resin is *modified* to form an oil-soluble material that may be heat-hardened by the addition and use of metal resinates. The para-substituted phenol prevents cross linking of the polymer chains. Straight-chain polymers are usually soluble in oils or other solvents; cross-linked polymers are very insoluble. These resins offer a very wide variety of protective surface coatings that are very hard, nonporous, elastic, and unaffected by heat or the usual solvents.

Protein resins are obtained by treating various protein materials with formaldehyde. This treatment causes a hardening of the protein to form a plastic material and also converts the protein into a material that is not subject to putrefaction. The exact nature of the chemical changes involved is not known definitely. The outstanding characteristic of this type of plastic is its easily polished surface.

Historical and General Description of Various Types.—Even though plastic materials had been known for almost 100 years, the industry was not well established until the early part of this century. Numerous investigators studied the phenomena of polymerization and condensation for resin formation, but L. H. Baekeland was the first man to develop scientific control and to produce commercial phenolic resins (1909). His discovery stimulated tremendously the search for new plastics and resulted in an increase of varieties by twenty fold and an increase in the use by a million fold. The production of plastics has grown more than 2,000 per cent[1] since Baekeland's invention.

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[1] WEITH, Plastics, *Ind. Eng. Chem.*, **31**, 557 (1939).

Recent research on plastics from agricultural materials[1] may open up a new field and a new application of chemurgy. (See Table 2 for a tabulation of the general properties of the various plastics.)

Cellulose nitrate, or pyroxylin, plasticized with camphor and introduced as Celluloid, was the first synthetic plastic of industrial significance. Even though it is a material hazardous to handle, readily decomposed by heat, and unstable to sunlight in the unpigmented form, it has many unique properties which long made it the best thermoplastic material available for many purposes. Even though the newer thermoplastics have many advantages over pyroxylin, it has shown a steady increase in production. Cellulose nitrate was first discovered about the middle of the nineteenth century and was first used as a plastic base in 1868 by John Wesley Hyatt while searching for an ivory substitute.

Cellulose acetate[2] was prepared in 1865 but the first mention in the literature of a plastic from this material did not appear until 1903. In 1906, Miles showed that the triester could be partly hydrolyzed to give an acetone-soluble material with better properties than the triester. No great commercial progress was made until the outbreak of the First World War, when a noninflammable lacquer was used for safe airplane wing coatings. Since 1931 cellulose acetate plastics have been keen competitors with the other plastic materials.

Cellulose ethers were first made and proposed as industrially useful products in 1912 in Germany, Austria, and France. Methyl cellulose was introduced in 1939 by the Dow Chemical Company. These ethers have not yet attained widespread consumption, but their properties and compatability with resins indicate that they will be increasingly sought after.

The first commercial synthetic resin, the *phenol-formaldehyde* condensation and polymerization product, was described and patented by Baekeland in 1909[3] in the United States. Although in 1872 Baeyer had reported that the reaction between phenol and formaldehyde led to resin formation, no products of commercial value were obtained until the work of Baekeland. He was the first to control this reaction scientifically. The original Bakelite Company was organized in 1910 and merged with itself the Condensite Company and the Redmanol Chemical Products Company in 1922 to form the Bakelite Corporation. At present the Bakelite organization is a unit of the Carbide and Carbon Chemicals

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[1] Sweeney and Arnold, "Plastics from Agricultural Materials," *Iowa Eng Expt. Sta., Bull.* 154 (1942).

[2] Kline, History of Plastics and Their Uses in the Automotive Industry, *Modern Plastics,* **17,** No. 8, 58 (1940).

[3] Baekeland, Insoluble Product of Phenol and Formaldehyde, U.S. Pats., 942699; 942700; 942808; 942809; Dec. 7, 1909.

TABLE 2.—PROPERTIES OF PLASTICS[a]

	Phenol-formaldehyde			Urea-formaldehyde	Vinyl chloride-acetate		Vinylidene chloride	Methyl methacrylate	Polystyrene	Cellulose acetate	Cellulose nitrate	Cellulose acetate-butyrate
	Molded	Laminated	Cast		Unplasticized	Plasticized						
Molding qualities	Excellent	....	....	Excellent	Good	Fair	Good	Good to excellent	Excellent	Excellent	Good	Excellent
Softening point, °F	None			None	140–158	. . . .	200–325	150–230	190–250	140–260	160–195	140–250
Water absorption, immersion 24 hr., per cent	0.1–1.3	0.3–9.0	0.01–0.5	1–3	0 05–4.0	.....	0.00	0.4–0.5	0.00	1.0–3.0	0.6–2.0	0.8–2.0
Burning rate	Very low			Very low	Nil	Nil	Nil	Slow	Slow	Slow	Very high	Slow
Effect of age	None	Improves mechanical properties	Hardens slightly	Hardens slightly	None	None	None	Practically none	Very slight	Slight		
Effect of sunlight	Light shades discolor	Lowers surface resistance	Colors may fade	None	Darkens	Slight	Slight	Very slight	Yellows slightly	Slight	Discolors and becomes brittle	Slight
Effect of weak acids	Slight			Slight	Resistant	None	None	Practically none	None	Slight		
Effect of strong acids	Decomposed by oxidizing acids			Decomposed	Resistant	None	None	Affected by oxidizing acid	None	Decomposes		
Effect of weak alkalies	Slight			Slight	Resistant	None	None	Practically nil	None	Slight		
Effect of strong alkalies	Decomposes			Decomposes	Resistant	None	None	Practically nil	None	Decomposes		
Effect of organic solvents.	None			None	Soluble in ketones and esters		Highly resistant	Soluble in ketones, esters and aromatics	Soluble in aromatics and chlorinated hydrocarbons	Soluble in ketones and esters		
Machining qualities	Fair	Good	Excellent	Fair	Good		Good	Excellent	Fair to good	Good		
Clarity	Transparent, translucent, opaque	Opaque	Transparent, translucent, opaque	Translucent, opaque	Transparent to opaque		Transparent to opaque	Transparent	Transparent	Transparent to opaque		
Color possibilities	Limited	Limited	Unlimited	Unlimited, pastel shades	Unlimited		Unlimited	Unlimited	Unlimited	Unlimited		

[a] Adapted from "Plastics Catalog," 1943.

Corporation. These phenolic resins were applied to automobile parts as early as 1917. In 1921 nonmetallic gears made of laminated phenolic resins appeared on the market. After the original Baekeland patents expired in 1926 and 1927, new companies were formed to make phenolic resins and the industry grew rapidly.

Cast phenolic resins were introduced about 1929 by the American Catalin Corporation, but it was not until about 1932 that any great production developed. These cast resins offer a wider range of colors than is possible with the regular phenolic resins wherein the reaction is carried farther and destroys or masks pastel shades.

The condensation of urea with formaldehyde to form resinous products was discovered in 1897. In 1930 *urea-formaldehyde* molding powders made their appearance on the market and extended unlimited color possibilities to the field of thermosetting resin plastics. The first composition was in the form of transparent sheet to take the place of glass but it tended to crack too easily. Research by Carleton Ellis showed that this cracking could be minimized or eliminated by the addition of a hygroscopic filler.[1] The Toledo Scale Company sponsored research at the Mellon Institute to develop a urea resin to replace porcelain-on-metal scale covers. The result of this research brought into being the Plaskon Company.

The polymerization of acrylic acid derivatives was noted as early as 1872. Much of the fundamental work was done by Rohm, who, in 1901, published his studies on the polymers and molecular weight of acrylates. In 1931 the Rohm and Haas Company began limited commercial production of *acrylates* under the name Plexiglas. When the Du Pont Company entered the market in 1937 with polymers of methacrylic esters, this field of water-clear transparent plastics grew very rapidly. These resins have singular optical properties that suggest innumerable applications.

Alkyd resins result from the interaction of polybasic acids and polyhydric alcohols. Berzelius, in 1847, reported that tartaric acid and glycerine reacted to form a resin. It was not until 1901 that a resin was discovered from the fusion of phthalic anhydride and glycerine. The General Electric Company conducted extensive research in this field of plastics with the idea of making improved synthetic surface coatings and insulating varnishes. They marketed glycerol-phthalic anhydride resins —shortened to alkyd resins—under the name Glyptal. The alkyd resins are used chiefly in synthetic surface coatings.

Vinyl Resins.—In 1838, it was found that vinyl chloride in a sealed tube exposed to sunlight yielded a white precipitate. Many years later, in 1917, the polymerization of vinyl acetate in the presence of peroxides was recorded. Ostromislensky described the preparation of vinyl chloride in 1927, the same year that polyvinyl acetate appeared commercially in Germany. The vinyl acetals, formed from hydrolyzed polyvinyl acetate and aldehydes, were patented in 1934 and were claimed to be harder, tougher, and stronger than the original polyvinyl ester resins. Vinylidene chloride resins were developed most recently by the Dow Chemical Company in 1939. The latest developments in 1941 were the uses of this material in tubing to replace copper, brass, and stainless steel, under the name Saran. To date, the vinyl resins are used most extensively for safety glass, electrical insulation, chemical-resistant fabrics, and the like.

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[1] KLINE, *op. cit.*

Polystyrene is one of the oldest synthetic resins. It has been known since 1839, but it was first introduced into the United States in 1933 as a varnish for radio equipment. Commercial production of this plastic material was begun by the Dow Chemical Company about 1937.

Coumarone-indene resins[1] were among the early synthetic resins produced commercially in the United States. In 1890 coumarone and indene were isolated from certain coal-tar light-oil fractions and polymerized to form resinous products. Commercial production was begun about 1919 by the Barrett Company. These resins are used most extensively in combination with waxes, natural and synthetic resins, bitumens, and rubber.

Casein plastics[2] are the result of interaction of casein, a protein material, and formaldehyde. This material was patented in Germany in 1897 by a chemist who realized the commercial possibilities of this hornlike substance. These plastics were first produced commercially in the United States about 1919; but the industry has not been on a very economical basis because of the susceptibility to variation in climatic conditions, the lengthy manufacturing process, and the inability of casein plastic to be fabricated by automatic machinery.

Shellac,[3] a resin of natural organic origin from India, has been consumed as a plastic material since earliest times. Contemporary with Hyatt's discovery of Celluloid in 1868, patents were issued covering shellac in molding compositions. The first notable application of a shellac molding composition was in 1890 for phonograph records. By 1900 shellac was used extensively for molded electrical insulation and today enters into the manufacture of high-voltage insulators.

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[1] "Plastics Catalog," p. 174 (1943).

[2] "Plastics Catalog," p. 170 (1943). Other protein plastics are described by Brother, McKinney and Suttle, Protein Plastics from Soybean Products, *Ind. Eng. Chem.*, **32**, 31, 1648 (1940); Swallen, Zein, A New Industrial Protein, *Ind. Eng. Chem.*, **33**, 394 (1941).

[3] "Plastics Catalog," p. 168 (1943).

TABLE 3.—RESINS CLASSIFIED BY COST[a]

Type	Average Sales Price Per Lb. of Net Resin in 1937
Cast phenolic	$0.41
Tar acid resins	
For molding	0.18
For laminating	0.13
For coatings	0.17
Alkyd	0.20
Urea	0.45
Vinyl	0.69
Acrylate[b]	1.66
Polystyrene	0.72

[a] U.S. Tariff Commission, "Synthetic Resins," *Report* 131 (1938).

[b] In 1938, acrylate molding powder was $0.85 per pound and the cast resin was $1.25 per pound.

TABLE 4.—SYNTHETIC RESINS: UNITED STATES PRODUCTION AND SALES IN 1941[a]

Product	Production lb.	Sales		
		Pounds	Value	Unit value
A. Resins derived from coal tar:				
Total	339,200,666	255,721,097	$66,619,834	$0.26
Alkyd resins: total phthalic anhydride	128,362,566	63,372,053	12,475,807	0.20
Derived from tar acids:				
Cresol or cresylic acid	22,717,921	17,312,666	6,259,363	0.36
Phenol,				
For casting	6,661,760	7,018,797	3,436,711	0.49
For molding	41,333,155	40,941,741	12,978,878	0.32
For other purposes	50,645,064	49,484,635	9,209,865	0.19
Phenols and cresols	39,959,533	34,974,799	17,331,685	0.50
Xylenols	309,662	321,780	57,726	0.18
All others	49,211,005	42,294,626	4,869,799	0.12
B. Resins from noncoal-tar sources:				
Total	103,599,021	92,586,373	50,636,117	0.55
Maleic anhydride	9,473,995	8,357,314	1,117,625	0.13
Urea	34,848,718	33,370,720	10,797,582	0.32
All others	59,276,308	50,588,339	38,720,910	0.77
Total for resins, 1941	437,799,687	348,307,740	117,255,951	0.34
Total for resins, 1940	276,814,363	201,099,650	59,368,339	0.30
Total for resins, 1939	213,027,548	163,296,637	39,011,486	0.24
Total for resins reported 1938[b]	130,358,652	101,828,188	22,871,974	0.22

[a] *Modern Plastics*, **20**, No. 1, 86–87 (1943).

[b] Does not include resins from adipic acid, indene, coumarone, hydrocarbons, styrene, succinic acid, sulfonamides.

Wood contains about 30 per cent lignin, the binder for cellulose. Lignin forms resinous substances when heated with phenols, formaldehyde, and amines. In 1937 the first *lignin plastic* suitable for laminating became available. The development of lignin plastics of both thermoplastic and thermosetting types was announced in 1939.

TABLE 5.—WARTIME PRODUCTION OF PLASTICS[a]
(Including plastic materials used in lacquers and coatings)

Product	Millions of pounds	Product	Millions of pounds
Phenolics	152	Cellulose acetate-propionates Cellulose acetate-butyrates Ethyl cellulose	36
Alkyds	170	Styrenes	21
Urea-formaldehydes	100	Vinyls	123
Cellulose nitrates	60	Coumarone-indenes	55
Cellulose acetates	55	Acrylates	37

[a] RAYNOLDS, Inter-relationship of Plastics and Chemicals, *Chem. & Met. Eng.*, **51**, No. 3, 109 (1944).

TABLE 6.—NUMBER OF MANUFACTURERS ASSOCIATED WITH THE PLASTICS INDUSTRY AND THE CAPITALIZATION PER GROUP[a]

Capitalization	Plastics manufacturers	Plastics fabricators				Plastics equipment and supplies
		Cast resins	Laminated	Pyroxylin	Molded	
Over $1,000,000	24	2	14	13	43	35
500,000	5		1	6	6	16
300,000	2	2	2	5	14	11
100,000	3	6	3	10	27	27
50,000	3	7		2	19	11
25,000	1	8	1	4	16	8
10,000		3	1	4	7	4
5,000		2		2	6	2
No estimate	6	23	2	4	43	4
Total	44	53	24	50	181	118

[a] *Ind. Eng. Chem.*, **31**, 562 (1939).

Uses and Economics.—The uses to which plastics are put depend upon the application and the properties of the various molding compositions. Much has already been presented in this chapter regarding the multitudinous applications of these products. The most important of these are listed under the manufacture of each type of plastic. Perry[1] tabulates dimensions of pipe and tubing made from resins.

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[1] PERRY, *op. cit.*, pp. 916–918.

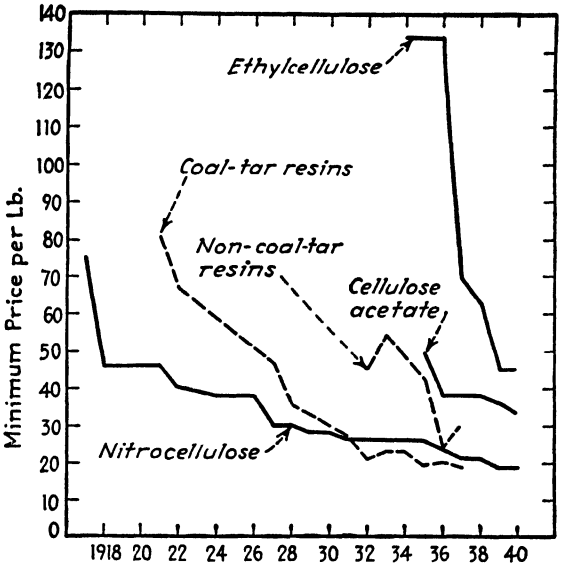

FIG. 1.—Price trends in plastics and resins.

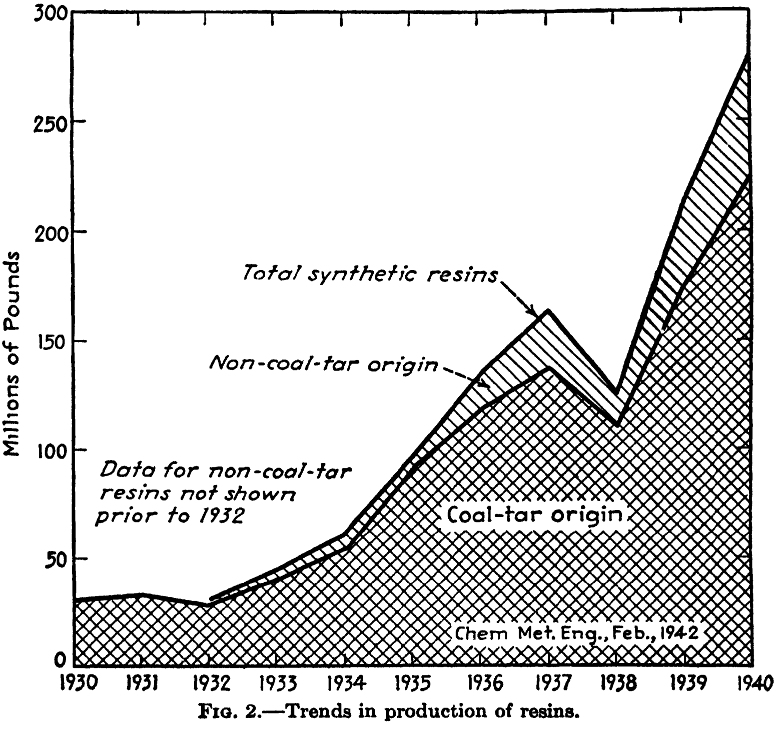

FIG. 2.—Trends in production of resins.

Table 3 shows the relative cost of the various plastics, Table 4 the United States production in 1941, and Table 6 the number of manufacturers associated with this industry. Plastics represents one of the fastest growing industries in the United States.[1] There has been a very great increase in plastics production during the Second World War, as shown by the estimates of Table 5.

Raw Materials.[2]—The plastics industry has grown so rapidly that the industries supplying the basic and intermediate raw materials have been unable to keep pace with it because of lack of sufficient, ready raw materials and process equipment. These basic and intermediate raw materials come from all parts of the nation—mines, forests, farms, quarries, paper and textile mills, cotton plantations, and natural gas and petroleum fields. The coal mines supply the basic needs for phenol, formaldehyde, dyes, solvents, maleic and phthalic anhydrides, and many other organic chemicals. The forests supply the lumber for wood-flour fillers and for some few chemicals. The farms are the basis for lactic acid from milk or corn sugar, bean meal from soy plants, glycerine from fatty oils, and the like. The quarries supply asbestos and other mineral fillers, limestone for calcium carbide, and ultimately for acetylene and vinyl resins. The paper and textile mills provide paper products and fabrics for laminated plastics. The cotton plantations grow cotton and linters for

TABLE 7.—CLASSIFICATION OF FILLERS

Organic Origin	Inorganic Origin
Cellulosic:	Mineral fillers:
Wood flour	Asbestos
Cotton	Powdered mica
α-Cellulose	Silicate clays, talc, kieselguhr
Paper pulp	Barytes
Shredded textiles	Whiting
Bagasse, corn husks, seed hulls, etc.	Pumice, emergy
	Zinc and lead oxides
	Cadmium and barium sulfides
Carbonaceous:	
Graphite	Powdered metals:
Carbon black	Iron
	Lead
Miscellaneous:	Copper
Powdered rubber	Aluminum
Plasticizers	

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[1] BATTERS and LEE, How Much Can Plastics Production Be Expanded? *Chem. & Met. Eng.*, **48**, 128 (1941).

[2] RAYNOLDS, Inter-relationship of Plastics and Chemicals, *Chem. & Met. Eng.*, **51**, No. 3, 109 (1944), very informative; ESSELEN and BACON, *op. cit.;* WEITH, *op. cit.;* OTT, Cellulose Derivatives as Basic Materials for Plastics, *Ind. Eng. Chem.*, **32**, 1641 (1940); SWALLEN, *op. cit.;* SWEENEY and ARNOLD, *op. cit.*

cellulose esters and ethers. The natural gas and petroleum fields furnish hydrocarbons and other chemicals for resins, solvents, asphalts, and very many industries.

Plastics are made from molding compositions which are prepared from two or more of the following raw-material groups:

Binder.—This is usually a resin or cellulose derivative.

Filler.—Cellulose, wood flour, cotton fiber, asbestos, mica, or fabrics may be added to increase strength. These are classified in Table 7.

Plasticizer.[1]—Plasticizers are added to cellulose derivatives and to certain thermoplastic resins to produce tough, resilient products of varying properties. These plasticizers may be camphor, phthalates, glycol esters, glycol ester-ethers, phthalyl glycollates, or fire retardants such as triphenyl and tricresyl phosphates.

Dyes and Pigments.—The dyes used vary in resistance to sunlight and to the plastic binder. The colors employed are the triphenylmethane basic dyes, azo dyes, and anthraquinone vat dyes (*cf.* Table 8).

Catalyst.—The thermosetting resins may use either an acid or basic catalyst depending upon the desired properties, while the resins of the vinyl group may use peroxides to initiate the polymerization of the monomers.

Lubricants.—Lubricants, such as stearates and metallic soaps, are used particularly in cold-molding compounds to facilitate the molding operation.

THERMOSETTING RESINS

Phenolic Resins (Molding Type).—The phenolic resins comprise the largest group of plastics and are of coal-tar derivation. They may be made from almost any phenolic body and an aldehyde such as formaldehyde or furfural. The resinous product obtained from the condensation of phenol and formaldehyde depends primarily on the concentration of the reactants, the nature of the catalyst used, the time of reaction, and the temperature. The outstanding properties of these resins are excellent heat resistance, water resistance, resistance to chemicals, moldability, and electrical insulating qualities. They do, however, lack color stability. They are used for automotive and aircraft parts, electrical insulation, corrosion-resistant apparatus, radio cabinets and parts, as well as for telephone equipment.

The molding-type phenolic resins are of the "two-step" variety.[2] An acid catalyst is used for the reaction of a limited amount of formaldehyde

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[1] VAN ANTWERPEN, Plasticizers, *Ind. Eng. Chem.*, **34,** 68 (1942).

[2] CALLAHAM, Modern Plant Makes Phenolic Resins at Springfield, *Chem. & Met. Eng.*, **48,** No. 6, 88 (1941); *Chem. & Met. Eng.*, **46,** 519 (1939) pictured flow sheet; ANON., Spray Drying Speeds Resin Production, *Chem. Industries*, **54,** 54 (1944).

TABLE 8.—GENERAL PROPERTIES OF COLORING MATERIALS USED IN PLASTICS[a]

Type	Affinity	Hue	Dispersibility in resins	Fastness properties		Uses
				Light	Alcohol and water	
Acid dyes	Direct for proteins	Bright and strong	Generally poor	Good	Bleed	Protein plastics, cast phenolics, urea resins
Mordant dyes	Direct for proteins	Somewhat dull	Generally poor	Very good	Bleed	Same as acid dyes
Basic dyes	Proteins, certain clays, high tannin cellulosic materials	Very bright and strong	React with many resins. Good	Poor	Bleed	Can be applied to most plastics Not much used in hydrocarbon products
Direct and developed dyes.	Cellulosic materials	Somewhat dull	Generally poor	Moderate	Bleed	Used to color cellulosic materials and water-soluble binders
Sulfur dyes	Cellulosic materials	Dull	Poor	Good	Good	Used chiefly for rubber tire fabrics and trubenized cloth
Vat dyes	Cellulosic materials	Somewhat dull and weak	Moderate	Very good	Good	Useful in many plastics. Expensive
Acetate dyes	Cellulosic acetates	Bright	Moderate	Moderate	Bleed	Cellulose acetate fabrics and sheets
Colors and lakes	All materials by adhesion	Bright	Good	Moderate to good	Many bleed	Resins and cellulose esters
Pigments	All materials by adhesion	Soft toned, dull	Good	Very good	Good	All opaque plastics
Spirit-soluble colors	All materials by absorption or adhesion	Bright and strong	Good	Varying	Bleed	Most plastics that tolerate alcohol in processing
Oil-soluble colors	All materials by absorption or adhesion	Bright and strong	Good	Moderate	Bleed	Resins and cellulose esters and hydrocarbon plastics

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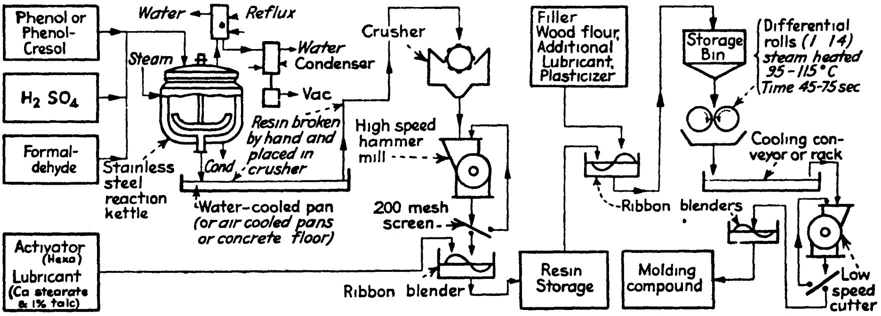
[a] Adapted from "Plastics Catalog," p. 145 (1941).

with excess phenol. The resulting thermoplastic resin is later mixed with more aldehyde in the presence of a basic catalyst such as hexamethylenetetramine, known in this industry as *hexa.* Figure 3 and the following description show the coordinated sequences of *unit operations* (Op.) and *unit processes* (Pr.) for the production of this type of resin.

The phenol and formaldehyde are placed in the reaction kettle with the catalyst (sulfuric acid) and heated 3 or 4 hr. at a temperature of 285 to 325°F. (Pr.).

During the *condensation,* reaction water is eliminated and forms the upper of two layers. This water of reaction is removed under vacuum without the addition of heat so that the fusible resin will not cure or set up in the kettle (Op.).

The warm, dehydrated, viscous resin is run out of the kettle into shallow trays and allowed to cool and harden. The cooled, brittle resin is crushed, finely ground, and becomes the resin binder for molding phenolic resins (Op.).


Phenol or Phenol-Cresol
H_2SO_4
Formaldehyde
Activator (Hexa) Lubricant (Ca stearate & 1% talc)
Water
Reflux
Steam
Water
Condenser
Vac
Stainless steel reaction kettle
Cond
Resin broken by hand and placed in crusher
Water-cooled pan (or air cooled pans or concrete floor)
Crusher
High speed hammer mill
200 mesh screen
Ribbon blender
Filler Wood flour, Additional Lubricant, Plasticizer
Resin Storage
Ribbon blenders
Storage Bin
Differential rolls (1 14) steam heated 95-115°C Time 45-75 sec
Cooling conveyor or rack
Molding compound
Low speed cutter

For a Typical Molding Compound

Phenol	42 lb	Hexa	3 7 lb
Formaldehyde	27 lb	H_2SO_4	0 1 lb
Wood flour	52 lb	Black dye (Nigrosin)	1 3 lb
		Ca Stearate	0 7 lb

Per 100 lb finished molding compound

FIG. 3.—Flow sheet of molding compound of the phenol-formaldehyde type.

The crushed and ground resin is blended with the activator (hexamethylenetetramine, "hexa") (Op.).

Phenolic molding compounds are made into articles by compression molding. The powder, mixed with fillers, lubricant, and plasticizers, is further reacted on steam-heated rolls, cooled, and ground (Pr.). This molding powder is placed in hardened steel molds under a temperature of 280 to 350°F. and a pressure from 2,000 lb. per sq. in. upward (Op. and Pr.).

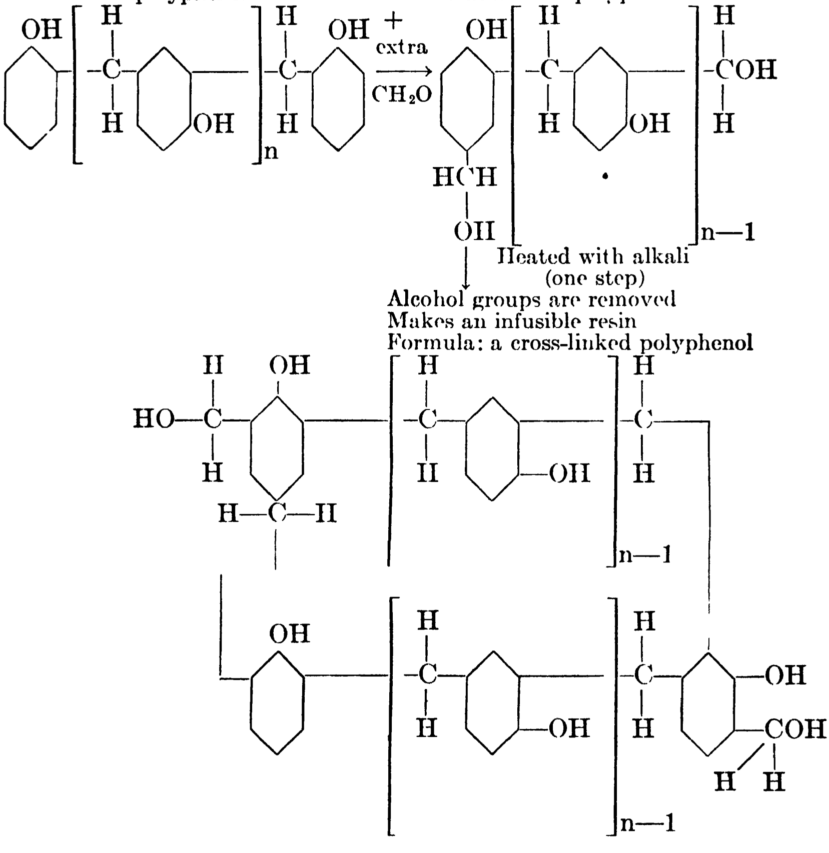
The final chemical polymerization reaction, or cure, which takes place in the mold to transform the powder into a rigid, infusible shape, requires 30 sec. to 10 or 12 min. depending on the class of the molding powder and the size and shape of the finished article.

Recently (1943) the heatronic molding process has been announced by the Bakelite group as an improvement in the molding or curing of plastics. This is particularly applicable to the molding of articles with a thickness of over ⅜ in. which are pressed as usual then heated to the necessary 320°F. by employing a high-frequency current as the source of the heat. This new method of curing causes the reactions to take place in less time and with much more uniform results.

The probable reaction and constitution of the resin are given as follows by Bender and reported in an article by Butler:[1]

PHENOL-FORMALDEHYDE
REACTIONS: CONDENSATIONS AND POLYMERIZATIONS

Phenol > 1: formaldehyde 1	Formaldehyde > 1: phenol 1
Any catalyst but generally acid	Any catalyst but generally alkaline
A fusible resin (two-step)	Makes first a fusible resin
Formula: a chain polyphenol	Formula: a chain polyphenol-alcohol



Heated with alkali (one step)

Alcohol groups are removed

Makes an infusible resin

Formula: a cross-linked polyphenol

Phenolic Resins (Cast Type).—This type of phenolic resin is made by the direct or one-step process. The properties vary somewhat from those of the molded phenolic variety. It is possible to prepare these in a wide range of color, transparency, or opacity largely because the resinification reaction or the curing is not carried to the completion desired in the ordinary infusible and insoluble phenol-formaldehyde resins. In addition they are readily machinable, have high tensile and impact strengths, and are nonflammable. Some of the more important uses are for industrial cabinet housings, novelties, decorative articles, interior lighting fixtures, adhesives for wood veneers and grinding disks, kitchen utensils, and handles. The phenol and formaldehyde with a basic catalyst (usually barium hydroxide or caustic soda) are placed in a nickel or stainless-steel reaction kettle and heated at the boiling point to as low as 160°F. for a period of 10 min. to 3 hr. The longer time at the lower temperature permits better control (see Fig. 4). The heat of reaction liberates 159 B.t.u. per lb. of reactants.[1] Hence it is necessary at certain phases of the reaction to cool by means of water in the jacket. During the reaction, water separates as the upper layer, and the mixture darkens slightly and increases in viscosity. The degree of reaction is controlled by means of time, temperature, pH readings, and viscosity determinations. During the removal of about 75 per cent of the water under vacuum, the resin becomes sirupy. At the proper time while the resin is still hydrophilic, an organic acid (lactic acid, phthalic anhydride, or maleic acid) is added to neutralize the resin and to clarify the color. If the resin is still hydrophilic, after neutralization the now four-component resin should not separate from the remaining water when cooled to 75°F. If a translucent resin is desired, glycerine is added to the four-component resin after the lactic acid addition on the basis of 130 lb. per 1,000 lb. of phenol. Before the final dehydration of the resin, plasticizers, pigments, and colors are added to the kettle and mixed with the resin. Dehydration is effected under vacuum at a resin temperature not in excess of 165 to 175°F., and the hot resin is withdrawn and poured into preheated lead molds. The final reaction and hardening take place by curing the resin

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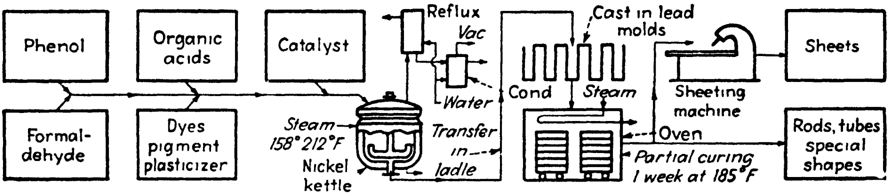
[1] BUTLER, Phenol Resins and Resin Emulsions, *Am. Dyestuff Reptr.*, **32**, 128 (1943); POWERS, "Synthetic Resins and Rubbers," pp. 60–68, review of structure theories, John Wiley & Sons, Inc., New York, 1943.



Phenol		1000 lb	To produce 1600-1,675 lb of opaque cast phenolic resin, for translucent resin add 130 lb glycerine increasing yield to 1730-1,800 lb
Formaldehyde	37 %	1,750 lb	
Caustic soda.	100 %	25 lb	
Lactic acid	50 %	135 lb	

FIG. 4.—Flow sheet for cast phenol-formaldehyde type resin.

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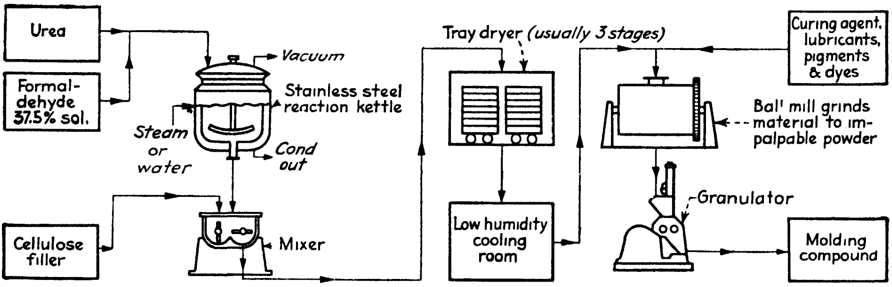
[1] "Plastics Catalog," p. 95 (1943).

in the molds at 185°F. for periods up to 5 days. The curing ovens are heated with steam under precise temperature control.

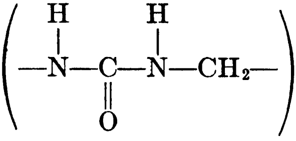
The molds used in the casting of these resins are either single molds or the split type and may be made of lead or rubber backed with plaster of paris. The castings are so made that the finished product is obtained by one or more standard machining operations[1] including slicing, sawing, cutting, drilling, threading, forming, carving, embossing, turning, milling, and polishing.

Urea-formaldehyde Resins.[2]—When urea is condensed with formaldehyde, water-soluble, water-white intermediates are formed, which have been identified as monomethylol urea, $NH_2 \cdot CO \cdot NHCH_2OH$, and dimethylol urea, $CH_2OHNH \cdot CO \cdot NHCH_2OH$. Urea and formaldehyde, with some ammonia to control pH, react under controlled time and temperature, 60 to 100°C. (see Fig. 5). These intermediates are used in admixture with some form of cellulose such as paper, pulp, or rayon before the final reaction and curing to an infusible, insoluble product. The structural unit of this product may be represented


Urea
Formaldehyde 37.5% sol.
Steam or water
Vacuum
Stainless steel reaction kettle
Cond out
Cellulose filler
Mixer
Tray dryer (usually 3 stages)
Low humidity cooling room
Curing agent, lubricants, pigments & dyes
Ball mill grinds material to impalpable powder
Granulator
Molding compound

Urea	42 Lb	Cellulose filler	40 Lb	To produce 100 Lb
Formaldehyde	42 Lb	Curing agent, lubricant and dye	18 Lb	Molding compound

FIG. 5.—Flow sheet of molding compound of the urea-formaldehyde type.



$$\left(\begin{array}{c} \text{H} \quad\quad \text{H} \\ | \quad\quad\quad | \\ -\text{N}-\underset{\underset{\text{O}}{\|}}{\text{C}}-\text{N}-\text{CH}_2- \end{array}\right).$$

The final curing takes place in the presence of suitable catalysts and at a controlled temperature. In combination with finely divided α-cellulose, these resins are available as molding powders or granules. This material is compression-molded at temperatures from about 285 to 315°F. and at pressures varying from 3,000 to 6,000 lb. per sq. in. The rate of setting or polymerization depends on the temperature used, the curing agents present, and the form of the finished part. The outstanding properties are unlimited translucency or opacity, excellent light diffusion, rigidity, and lack of odor and taste. These resins are used for closures, lighting reflectors, tableware, buttons, and baking enamels.

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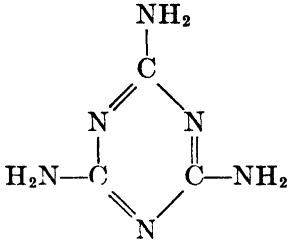
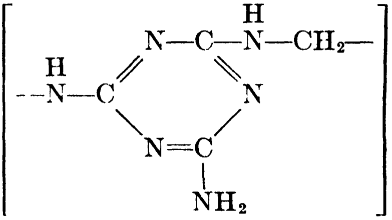
[1] "Plastics Catalog," pp. 94, 280 (1943).

[2] "Plastics Catalog," pp. 105, 282 (1943); BROTHMAN and WEBER, Design of a Urea Resin Plant, *Chem. & Met. Eng.*, **48**, 73 (1941).

Melamine Resins.—These are formed by reacting melamine with formaldehyde to yield water-white, water- or water-alcohol-soluble intermediates. Melamine is obtained from dicyandiamide and is usually considered to have the following formula:



The structural unit of the resin is represented as



Molded or laminated parts made from melamine resins are extremely hard and resistant to abrasion. Molding powders made from these resins are molded by compression. The rate of curing is dependent on the same variables that control the curing rate of the urea resins. The cured resins are colorless, resist hot water and organic solvents, and are heat-resistant.

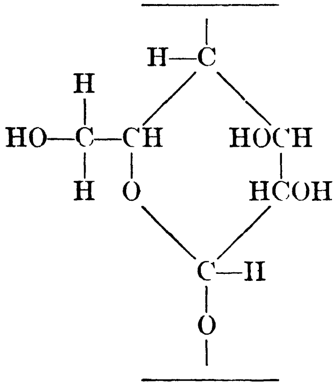
Alkyd Resins.—The resins grouped in this class are chiefly the reaction products from polybasic acids and polyhydric alcohols. However, the name of this class includes also those resins from polyhydric alcohols and polybasic acids that have been modified with fatty acids from vegetable oils, with rosin, and with other synthetic resins.

The reaction of glycerine or ethylene glycol with a polybasic acid like phthalic anhydride produces resinous products; when ethylene glycol is employed, the product is of a balsamlike appearance and is nonhardening; when glycerine is reacted, the product is thermosetting. Because most of this type of resin is made from glycerine and phthalic anhydride, the class is placed among the thermosetting resins. This thermoreacting quality is probably caused by cross linkages set up by more points of reaction of the glycerine. The introduction of modifiers, such as monobasic acids or monohydric alcohols, reduces the number of active points of reaction that play a part in forming cross links between linear polymeric chains and increases the solubility of the resin.

These resins are used chiefly in protective coatings rather than in molded plastics because of their poor moldability. When they are combined with urea resins, coatings of very superior gloss, hardness, and increased resistance are obtained. Particularly useful properties of these resins are long retention of initial good appearance, long exterior-exposure life on weathering, ease of application, solubility in relatively cheap solvents, high gloss, adhesion to metal, and quick drying or baking schedule.

THERMOPLASTICS BASED ON CELLULOSE

Cellulose is generally pictured as being composed of a chain of glucosidic units represented by the formula:



It is composed of long chains of these units which may number 3,000 to 3,500. These elongated chains and the reactions of the cellulosic polyhydric alcohol are responsible for the formation of tough, flexible, cellulosic plastics. The properties of the cellulose derivatives depend upon the substituent groups, the amount of substitution, the type of pretreatment, and the degree of degradation of the long chains into shorter lengths.

Cellulose Ester Plastics.[1]—Cellulose plastics are usually solid or colloidal solutions of esters in plasticizers. The esters are made by esterifying purified, pretreated cellulose with appropriate acids and acid anhydrides in the presence of catalysts under controlled temperature. Both inorganic and organic esters are available commercially. The most important are the nitrate, acetate, and a mixed acetate-butyrate. Flow sheets for the production of cellulose nitrates are given in Fig. 3 of Chap. XXII.

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[1] "Plastics Catalog," pp. 110–122, 290–291 (1943).

Fully *nitrated cellulose* is unsuited for a plastic base because of its explosive character. Hence there is made a partly nitrated product with a nitrogen content of about 10.5 to 11.5 per cent. This cellulose nitrate is placed in large kneading mixers with solvents and plasticizers and thoroughly mixed. The standard plasticizer is camphor, first used by Hyatt in 1868. The compounded mixture is then strained under hydraulic pressure and mixed on rolls with coloring agents. The material is pressed into blocks. Finally, the plastic is made into sheets or other shapes seasoned to remove the residual solvent and polished by pressing under low heat. Some of the outstanding properties of cellulose nitrate include toughness, water resistance, ease of fabrication, ease of cementing, clarity, colorability, and inflammability. It is used for fountain pens, golf-club parts, toys, novelties, toothbrush handles, and cutlery handles.

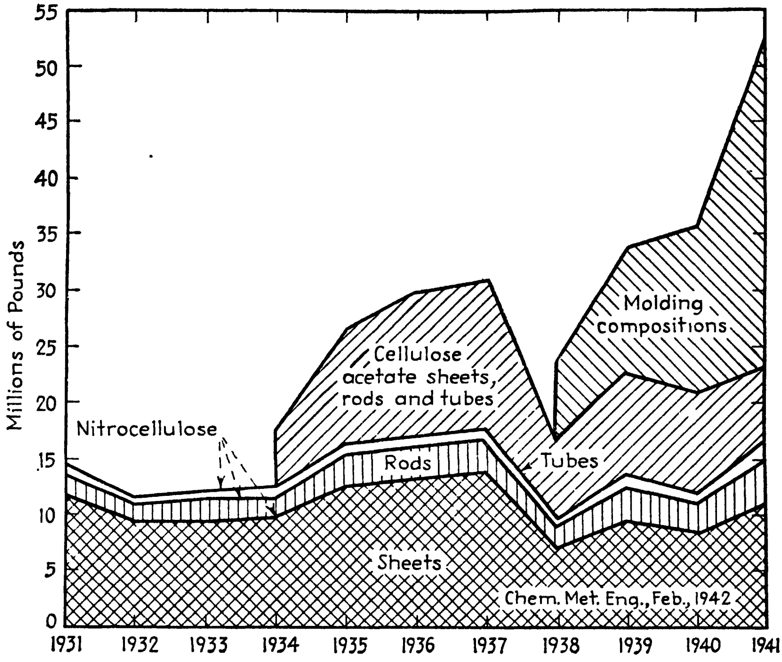


FIG. 6.—Trends in production of cellulose plastics.

Cellulose Acetate.—Fully acylated cellulose is partly hydrolyzed to give an acetone-soluble product, which is usually between the di- and tri-ester. This hydrolysis takes place in aqueous organic acids in the presence of a catalyst under controlled time and temperature. These cellulose organic esters are precipitated in a large volume of water, washed, filtered, and dried under controlled conditions of temperature and humidity. The esters are mixed with plasticizers, dyes, and pigments and processed in various ways depending upon the form of plastic desired (see Fig. 9, page 732).

These plastics may be fabricated by compression molding, injection molding, or continuous extrusion. Compression molding involves a temperature of 290 to 350°F. and a pressure of 2,000 to 5,000 lb. per sq. in. The material is cooled in the mold under pressure so that it can be handled without deformation when it is discharged from the mold. In injection molding, the material is heated to the temperature at which it will flow easily under a high applied pressure. The hot plastic is forced into a cold mold and the finished piece may be discharged from the mold immediately without further cooling.

The important properties of cellulose acetate include mechanical strength, impact resistance, transparency, colorability, fabricating versatility, moldability, and high dielectric strength. Some of its uses are as automobile steering wheels, airplane cockpit closures, electrical appliances, protective goggles, dials, control boards, and musical instruments.

Some of the noteworthy properties of *cellulose acetate-butyrate* are low moisture absorption, high dimensional stability, excellent weathering resistance, high impact strength, availability in colors, and improved finish. This plastic is used for exterior automobile lenses, furniture, refrigerators, hardware, gunstocks, and radio cases.

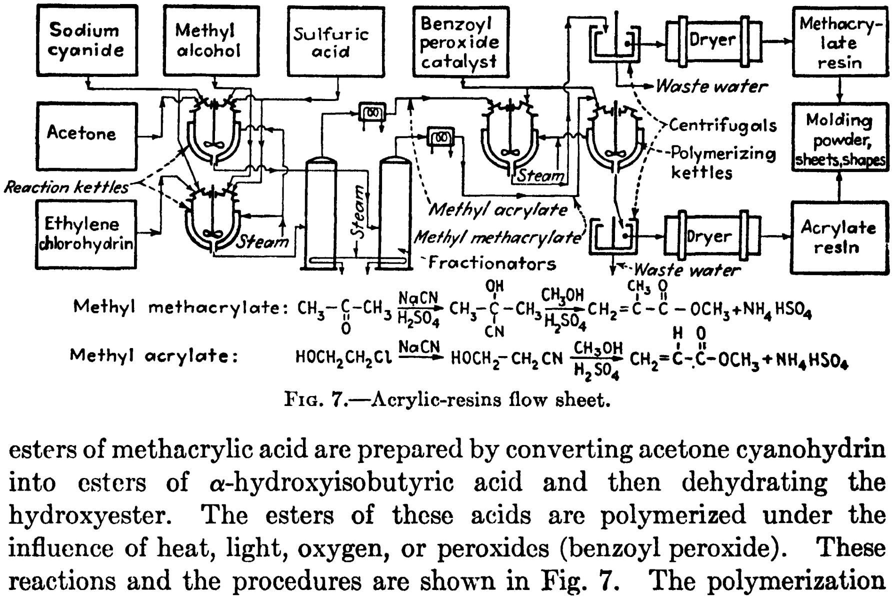
Ethyl Cellulose Plastics.—The base of these plastics is ethyl cellulose, a cellulose ether in which ethyl groups have replaced the hydrogen of the hydroxyl group. Commercial ethyl cellulose contains between 2.4 and 2.5 ethoxy groups per glucoside unit of the cellulose chain. The ethers are made by treating cellulose, such as wood pulp or cotton linters, with a concentrated solution of sodium hydroxide. The alkali cellulose formed is alkylated with such agents as ethyl chloride or ethyl sulfate. The alkylation must be carried out under carefully controlled conditions to prevent degradation of the cellulose chain and destruction of the alkylating agent. After the reaction is complete, the excess reagents are easily washed out. The ether is purified by washing it free from soluble materials. Ethyl cellulose is fabricated by injection molding or continuous extrusion. Some of its outstanding properties are unusually good low-temperature flexibility and toughness, wide range of compatability, stability to heat, thermoplasticity, and electrical resistance. It is often used for protective coatings, furniture, extrusion wire insulation, injection plastics, and rigid containers.

THERMOPLASTIC RESINS

Acrylic Resins.[1]—The esters of acrylic and methacrylic acids are of more importance at present for plastics than other derivatives of these acids that also form resinous products. The formula of acrylic acid is $CH_2{=}CH{-}COOH$, and the formula of methacrylic acid is

$$CH_2{=}C(CH_3){-}COOH.$$

The esters of acrylic acid are made through treating ethylene chlorohydrin with sodium cyanide. The cyanohydrin that is formed is converted to the ester by combined hydrolysis and esterification in the presence of concentrated sulfuric acid and the appropriate alcohol. The esters of methacrylic acid are prepared by converting acetone cyanohydrin into esters of α-hydroxyisobutyric acid and then dehydrating the hydroxyester. The esters of these acids are polymerized under the influence of heat, light, oxygen, or peroxides (benzoyl peroxide). These reactions and the procedures are shown in Fig. 7. The polymerization reaction is exothermic. The heat of polymerization[2] for the methyl ester has been determined as 8 cal. per g. The molecular weights of the polymeric esters vary with the conditions of manufacture, such as temperature, catalyst, catalyst concentration, and monomer concentration. The molecular weight decreases as temperature and catalyst concentration are increased. The polymers become softer, tougher, and more extensible as the molecular weight increases.



$$CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_3 \xrightarrow[H_2SO_4]{NaCN} CH_3{-}\overset{OH}{\underset{CN}{\overset{|}{\underset{|}{C}}}}{-}CH_3 \xrightarrow[H_2SO_4]{CH_3OH} CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}\overset{O}{\overset{\|}{C}}-OCH_3+NH_4HSO_4$$

$$HOCH_2CH_2Cl \xrightarrow{NaCN} HOCH_2{-}CH_2CN \xrightarrow[H_2SO_4]{CH_3OH} CH_2{=}\overset{H}{\overset{|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OCH_3+NH_4HSO_4$$

FIG. 7.—Acrylic-resins flow sheet.

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[1] "Plastics Catalog," pp. 130, 294 (1943); STRAIN, KENNELLY, and DITTMAR, Methacrylate Resins, *Ind. Eng. Chem.*, **31**, 382 (1939).

[2] DITTMAR, STRAIN, and KENNELLY, The Methacrylic Ester Resins, *Trans. Electrochem. Soc.*, **74**, 181 (1938).

This material may be fabricated by casting, compression molding, injection molding, or continuous extrusion. In casting, the monomers are polymerized by heat in the presence of a catalyst. Compression molding temperatures vary between 285 and 360°F., and the pressures are between 1,500 and 5,000 lb. per sq. in. Since these resins are thermoplastic, they should be cooled in the molds under pressure. For injection molding the conditions are 325 to 425°F. and 3,000 to 30,000 lb. per sq. in. Cast sheets and cast and extruded bars and rods may be shaped to order at temperatures of about 180 to 250°F. by the use of simple forms.

Outstanding properties of the acrylic resin plastics include superior transparency, dimensional stability, edge lighting, unlimited color range, water resistance, rigidity, and weather resistance. Some of the more important uses are as illuminating instruments (medical, surgical, and industrial), laminated glass interlayers, airplane windshields, dentures, artificial jewels, and furniture. Large amounts of the clear methyl methacrylic resin are employed for the eyepieces of gas masks, for watch glasses, and particularly for the transparent nose and blister windows in bombers and other airplanes.

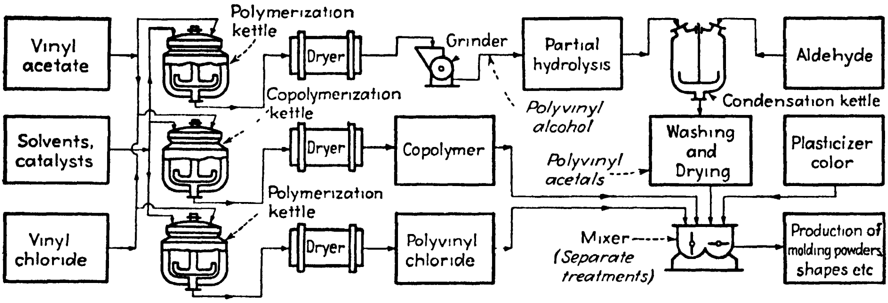
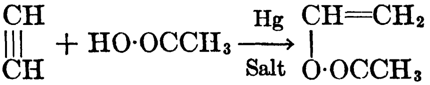


FIG. 8.—Vinyl-resins flow sheet.

Vinyl Resins.[1]—The polyvinyl resins are synthetic materials made from compounds having the vinyl ($—CH{=}CH_2$) group. The most important members of this class are polyvinyl acetate, polyvinyl chloride, the copolymer of the acetate and the chloride that combines the best properties of each one. Figure 8 illustrates the methods for preparing polyvinyl resins.

Vinyl acetate is a clear liquid the formation of which may be expressed:



$$\begin{matrix}CH\\ |||\\ CH\end{matrix} + HO\cdot OCCH_3 \xrightarrow[\text{Salt}]{\text{Hg}} \begin{matrix}CH{=}CH_2\\ |\\ O\cdot OCCH_3\end{matrix}$$

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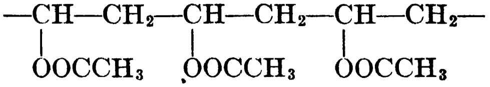
[1] "Plastics Catalog," pp. 153, 286 (1943); DOUGLAS, Vinyl Resins, *Ind. Eng. Chem.*, **32**, 315 (1940); TATOR, Between the Lines, *Chem. Industries*, **49**, 802 (1941); AKIN, Vinyl Resins in War and Peace, *Chem. Industries*, **52**, 456 (1943).

A flow sheet for this reaction is given in Chap. XXXIX, page 910. A copper salt is added to the monomer to prevent polymerization. This may be left behind by distillation. The monomer, a catalyst such as acetyl peroxide, and a solvent are placed in an autoclave, and some heat is applied. After a short induction period the polymerization begins and is allowed to proceed to a predetermined limit. Then the unreacted monomer and the solvent are removed. The polymer is a linear-chain compound which can be formulated in part as follows:



$$-\underset{\substack{|\\ \mathrm{OOCCH_3}}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{OOCCH_3}}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{OOCCH_3}}}{\mathrm{CH}}-\mathrm{CH_2}-$$

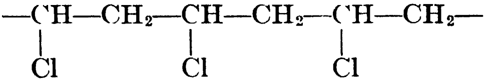
The dried polymer is ground and becomes the resin binder for molding compositions or a base for adhesives.

Under normal conditions, vinyl chloride is a gas that boils at −14°C. It may be made by the following reactions:

$$\mathrm{HC{\equiv}CH + HCl \rightarrow ClCH{=}CH_2} \tag{1}$$

$$\mathrm{CH_2{=}CH_2 + Cl_2 \rightarrow ClCH_2CH_2Cl \xrightarrow{Alkali} ClCH{=}CH_2} \tag{2}$$

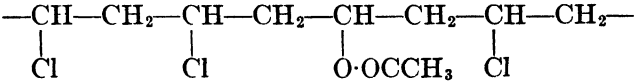
The monomeric vinyl chloride, like the vinyl acetate, is polymerized in an autoclave using a peroxide catalyst to give a polymer with a linear-chain molecule as follows:



$$-\underset{\substack{|\\ \mathrm{Cl}}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{Cl}}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{Cl}}}{\mathrm{CH}}-\mathrm{CH_2}-$$

This resin is always plasticized for use, whereas the polyvinyl acetate may or may not be plasticized.

A resin of more importance and wider use than either of the preceding is the copolymer of vinyl acetate and vinyl chloride. The monomers of both acetate and chloride are mixed with a solvent and catalyst and polymerized in an autoclave to yield a copolymer which might be represented in part as follows:



$$-\underset{\substack{|\\ \mathrm{Cl}}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{Cl}}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{O{\cdot}OCCH_3}}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{Cl}}}{\mathrm{CH}}-\mathrm{CH_2}-$$

Although the acetate:chloride ratio can be varied over wide limits to give resinous products suitable for a great variety of applications, the more important copolymers at present contain about 80 to 90 per cent of the chloride.

The properties of the preceding resins are closely associated with their average molecular weight and with the relative quantities of the polymers that make up the resin. For each ester type, the tensile and impact strengths, abrasion resistance, and viscosity in solution increase with higher molecular weights. The water absorption, refractive index, hardness, and electrical properties remain almost constant.

Examples of copolymerized vinyl acetate-vinyl chloride to show how the average molecular weight is varied to suit a particular application are listed as follows:

TABLE 9.—MOLECULAR WEIGHTS OF VINYL COPOLYMERS

Average Molecular Weight	Use
9,000	Surface-coating resin
10,000	Resin for calendar-coating paper or injection molding
12,500	Compression molding
15,500	Stiff sheet stock
21,000	Highly plasticized sheet and extruded wire coatings
22,000	Textile fiber

The polyvinyl acetate resin can be compression-molded at temperatures from 225 to 275°F. and pressures from 1,000 to 2,000 lb. per sq. in. Since the resin is thermoplastic, the molded piece should be cooled in the mold under pressure.

The polyvinyl chloride resin can be compression-molded at various temperatures and pressures depending on the amount and type of plasticizer present. In general, the temperatures and pressures are in the same range as those used to mold polyvinyl acetate. If this polymer is highly plasticized with tricresyl phosphate or dioctyl phthalate and then worked on rubber mills, it becomes a rubbery substance that is finding increasing use as a rubber substitute. It is not suitable for tires but has found wide application in raincoats and all types of insulating and jacketing materials.

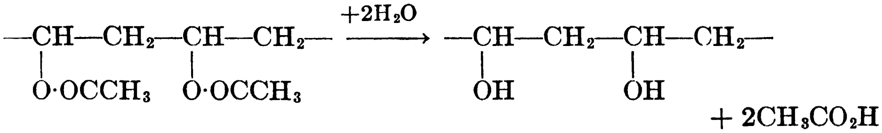
The copolymerized acetate-chloride is compression-molded at pressures from 1,200 to 2,000 lb. per sq. in. and temperatures from 250 to 290°F. Here again the piece should be cooled under pressure in the mold to about 90 to 100°F. This resin is injection-molded at 280 to 300°F. and at pressures from 15,000 to 22,000 lb. per sq. in.

Some outstanding properties and uses of these vinyl resins may be listed as follows:

1. *Vinyl acetate*—clear, adhesive, nontoxic, zero acid number, odorless and tasteless; used for molding compounds, adhesives, and plastic woods.
2. *Vinyl chloride*—resistant to water and chemicals, tough, nontoxic, odorless and tasteless; used for cable coverings, coated fabrics, tank linings, and as a rubber substitute.
3. *Copolymerized acetate-chloride*—nonwarping, nonshrinking, tough, strong, rigid, resistant to chemicals, nontoxic, odorless and tasteless, available in colors;

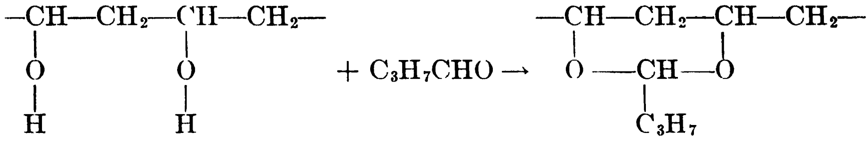
used for sound records, floor tile, pen parts, cable covering, belts and suspenders, raincoats, watch straps, and radio dials.

Vinyl Alcohol and Acetal Resins.—These resins are made from polyvinyl acetate which is first hydrolyzed to yield polyvinyl alcohol and then condensed with aldehydes to give a group of resins (or acetals), as shown in Fig. 8. The polyvinyl acetate is hydrolyzed under controlled conditions by either acid or alkali which replaces the acetyl groups with hydroxyl groups to yield polyvinyl alcohol.



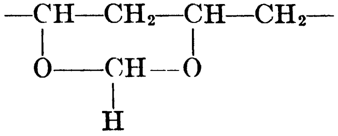
$$-\underset{\substack{|\\ \text{O·OCCH}_3}}{\text{CH}}-\text{CH}_2-\underset{\substack{|\\ \text{O·OCCH}_3}}{\text{CH}}-\text{CH}_2- \xrightarrow{+2\text{H}_2\text{O}} -\underset{\substack{|\\ \text{OH}}}{\text{CH}}-\text{CH}_2-\underset{\substack{|\\ \text{OH}}}{\text{CH}}-\text{CH}_2- + 2\text{CH}_3\text{CO}_2\text{H}$$

This method of preparation is used because polyvinyl alcohol cannot be prepared by direct polymerization as the monomer is an unknown compound. Vinyl alcohol, $CH_2{=}CHOH$, is the enol form of acetaldehyde, CH_3CHO, and is not stable. Polyvinyl alcohol is a unique plastic because it is plasticized by water and is completely soluble in an excess of water.[1] The polyvinyl alcohol reacts with an aldehyde under the influence of heat and in the presence of an acid catalyst, such as sulfuric or hydrochloric acid, and the result is a typical acetal. The polyvinyl butyral is shown as follows:



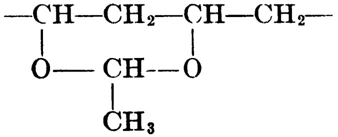
$$-\underset{\substack{|\\ \text{O}\\ |\\ \text{H}}}{\text{CH}}-\text{CH}_2-\underset{\substack{|\\ \text{O}\\ |\\ \text{H}}}{\text{CH}}-\text{CH}_2- + \text{C}_3\text{H}_7\text{CHO} \rightarrow \begin{array}{c} -\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2- \\ |\qquad\qquad | \\ \text{O}-\underset{\substack{|\\ \text{C}_3\text{H}_7}}{\text{CH}}-\text{O} \end{array}$$

In like manner, the corresponding formal and acetal are illustrated:



$$\begin{array}{c} -\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2- \\ |\qquad\qquad | \\ \text{O}-\underset{\substack{|\\ \text{H}}}{\text{CH}}-\text{O} \end{array}$$

Formal



$$\begin{array}{c} -\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2- \\ |\qquad\qquad | \\ \text{O}-\underset{\substack{|\\ \text{CH}_3}}{\text{CH}}-\text{O} \end{array}$$

Acetal

In actual commercial production, the hydrolysis and condensation reactions are never carried to completion because it has been found that the presence of residual acetyl and hydroxyl groups gives the resins some better properties.

The polyvinyl butyral[2] is usually extruded as a sheet for the interlayer for safety glass. Some of the polyvinyl acetals can be compression-molded at temperatures from 100 to 130°C. and injection-molded at temperatures from 170 to 190°C. The polyvinyl formals can be molded by either compression or injection, depending on the softening point.

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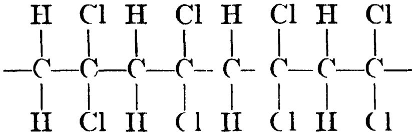
[1] Peierls, Polyvinyl Alcohol Plastics, *Modern Plastics*, **18**, No. 6, 53 (1941).

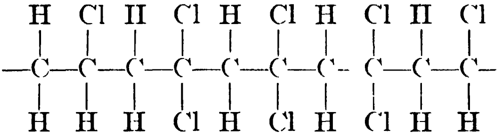
[2] "Plastics Catalog," p. 159 (1943).

Vinylidene Chloride Resins.[1]—This class of resins is one of the recent additions to the synthetic resin family. Based on unsymmetrical dichloro-ethylene, they were introduced in 1940 and may be formed by the polymerization of the monomeric vinylidene chloride, $CH_2{=}CCl_2$, to give resins which may be represented in part as



$$\begin{array}{ccccccccccccccccc} & H & & Cl & & H & & Cl & & H & & Cl & & H & & Cl & \\ & | & & | & & | & & | & & | & & | & & | & & | & \\ — & C & — & C & — & C & — & C & — & C & — & C & — & C & — & C & — \\ & | & & | & & | & & | & & | & & | & & | & & | & \\ & H & & Cl & & H & & Cl & & H & & Cl & & H & & Cl & \end{array}$$

or, the monomer may be copolymerized with vinyl chloride to give a new product represented as follows:



$$\begin{array}{ccccccccccccccccccccc} & H & & Cl & & H & & Cl & & H & & Cl & & H & & Cl & & H & & Cl & \\ & | & & | & & | & & | & & | & & | & & | & & | & & | & & | & \\ — & C & — & C & — & C & — & C & — & C & — & C & — & C & — & C & — & C & — & C & — \\ & | & & | & & | & & | & & | & & | & & | & & | & & | & & | & \\ & H & & H & & H & & Cl & & H & & Cl & & H & & Cl & & H & & H & \end{array}$$

The resins formed by copolymerization range from a flexible material having a softening point of about 70°C. to a hard, thermoplastic solid with a softening point of 180°C. Their higher softening point indicates a greater degree of crystalline character. If the fibrous crystals are not oriented, the vinylidene chloride resin has a tensile strength of 8,000 lb. per sq. in., which is an ordinary value. However, if the crystals are oriented by drawing, the tensile strength may be increased to about 60,000 lb. per sq. in. These resins may be fabricated by compression or injection molding or extrusion[2] with the use of specially developed techniques and equipment to get accurate control of properties and shapes.

Some noteworthy properties of these resins are high tensile strength, high fatigue and abrasion resistance, toughness, resistance to water and chemicals, nonflammability, high dielectric strength, ease of machining, and colorability. They are used for subway car seats, chair seats, fish leaders, and corrosion-resistant pipe.

Styrene Resins.[3]—Monomeric styrene is made by the pyrolysis of ethylbenzene, which is synthesized from ethylene and benzene. The factors that affect the polymerization of the monomer are the temperature and the purity of the styrene. Polymerization at moderate temperatures without catalysts produces resins which are of high average molecular weight and which impart high viscosity to their solutions. If the temperature is increased and catalysts such as benzoyl peroxide, oxygen, or stannic chloride are added, the average molecular weight and viscosity tend to decrease.

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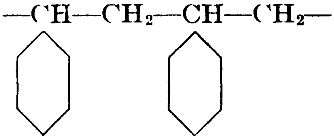
[1] "Plastics Catalog," p. 62 (1941). GOGGIN and LOWRY, Vinylidene Chloride Polymers, *Ind. Eng. Chem.*, **34,** 327 (1942); REINHARDT, Vinylidine Chloride Polymers, *Ind. Eng. Chem.*, **35,** 422 (1943).

[2] ANON., Extruding Vinylidene Chloride, *Modern Plastics*, **19,** No. 12, 33–39 (1942).

[3] WEITH, TURKINGTON, and ALLEN, Polystyrene, *Ind. Eng. Chem.*, **32,** 1301 (1940); "Plastics Catalog," pp. 165, 288 (1943).

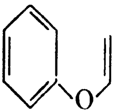
There is some uncertainty about the mechanism of the polymerization of styrene. It appears highly probable that the process may occur in at least three steps: chain initiation, chain propagation, and chain termination, and that the second step is very rapid compared to the first. In the light of recent investigations the configuration of the polymer is thought to be in the following head-to-tail form:



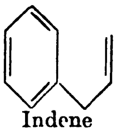
$$-CH-CH_2-CH-CH_2-$$

The lower polymers (20,000 to 30,000 average molecular weight and below) are brittle and have low mechanical strength. The higher polymers are strong and tough. This material can be compression-molded, but injection molding is preferred. The temperatures for injection molding are from 160 to 230°C. and the pressures from 10,000 to 30,000 lb. per sq. in. Some of the outstanding properties are low specific gravity, high index of refraction, excellent acid and alkali resistance, excellent water resistance, dimensional stability, low molding shrinkage, excellent molded finish, ability to carry light, excellent electrical properties, and transparency. Thus this resin is used for acid, base, and bleaching solution bottle closures, high-frequency radio and television parts, jewelry, signs, combs, and novelties.

Coumarone-indene Resins.[1]—Coumarone and indene occur in the 150 to 200°C. fraction which is obtained from coal-tar light oils recovered from by-product coking operations. These compounds are polymerized with concentrated sulfuric acid. The formulas of the two monomers are as follows:



Coumarone



Indene

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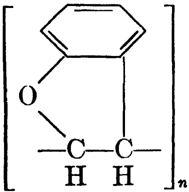
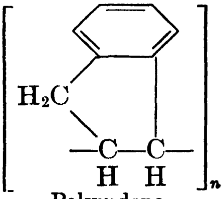
[1] "Plastics Catalog," p. 174 (1943).

The polymerization is assumed to be a chain reaction to give polymers of the following general patterns:

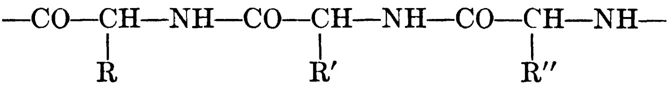

Polycoumarone


Polyindene

Regulation of the polymerization conditions produces resins from a viscous semifluid state to a hard, brittle solid. When these resins are hydrogenated in the presence of catalysts, a series of so-called *cycloparaffin resins* are obtained which are more compatible with waxes and aliphatic hydrocarbons than are the regular coumarone-indene polymers. These hydrogenated resins are much lighter in color than the regular resins, varying from a pale straw to water white. Some important properties of these resins are acid, alcohol, alkali, brine, and water resistance, high electrical breakdown, low power factor, neutral reaction, thermoplasticity, nonsaponifiability, low specific gravity, low viscosity in solution, and compatability with waxes, natural resins and derivatives, synthetic resins, rubber, and bitumens. They are used for rubber compounding, mastic floor tile, protective coatings, and transcription records.

PROTEIN PLASTICS

Casein Plastics.[1]—Casein plastic is the product of the reaction between casein and formaldehyde. Casein itself is a protein and recent X-ray studies have shown that proteins have a polypeptide structure.



$$\text{—CO—}\underset{\displaystyle R}{\text{CH}}\text{—NH—CO—}\underset{\displaystyle R'}{\text{CH}}\text{—NH—CO—}\underset{\displaystyle R''}{\text{CH}}\text{—NH—}$$

The dry process for the manufacture of the plastic is based on the plasticization of casein powder, containing about 40 per cent total moisture, by the simultaneous action of heat and pressure. The soft plastic is extruded as rods or tubes from screw cylinder presses such as are used in the rubber industry. If sheets are required, the rods are flattened in hydraulic presses to the desired size. The rods and sheets of soft plastic are then hardened in an aqueous bath of 4 per cent formaldehyde. The hardening period varies from 3 weeks to 6 months, depending on the size of the rod or piece. After hardening, the material is dried to a moisture content of about 8 to 12 per cent. The drying period is almost as long as the hardening period. Recent improvements, however, have greatly reduced the curing time. It has been found that, if alum is mixed with the water before extrusion or if the casein powder is treated with aqueous formaldehyde, the hardening begins at such a rate that the extruded material can be worked into various shapes and then hardened in the formaldehyde bath for only a few days. More recently, a thermoplastic molding composition has been made of formaldehyde-hardened protein material that comes finished from the mold.

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[1] Brother, Casein Plastics, *Ind. Eng. Chem.*, **32**, 31 (1940); Brother, McKinney, and Suttle, Protein Plastics from Soybean Products, *Ind. Eng. Chem.*, **32**, 1648 (1940); Swallen, *op. cit.;* "Plastics Catalog," pp. 171, 298 (1943).

Thermosetting molding powders can be made from protein materials by mixing the formaldehyde-hardened proteins with phenolic resins and wood flour. Such a protein may be oil-free soybean meal. The curing time is about the same as for the phenolic resins, and the strength is about the same. Some outstanding properties are colorability, nonflammability, ease of polishing, ease of machining, and low hygroscopicity. The chief use of these plastics is for buttons, but they also find some use as buckles, beads, and novelties.

MISCELLANEOUS PLASTICS

Shellac Compositions.[1]—Shellac is obtained from a resinous material secreted by an insect, *Laccifer lacca Kerr*, which is native to India. The insect produces the raw lac from glands located in its skin. The resin is a solid solution of several chemical compounds having similar structures. The lac consists of two materials: a hard and a soft resin. Shellac is a unique plastic resin because it shows properties of both thermoplastic and thermosetting resins. Heat curing increases the mechanical and electrical strength. The resin is compatible with phenolic resins so that a wide variety of molding compositions can be made.

Compositions are softened on steam tables at 225 to 250°F. They are molded by compression molding at temperatures from 250 to 275°F. and pressures from 1,000 to 3,500 lb. per sq. in. The molds must be cooled to 90 to 120°F. before the pressure is released. Injection molding at 230°F. can be carried out on a 1- or 2-min. cycle for many pieces. Some noteworthy properties of shellac compositions are low dielectric constant, high dielectric strength, arcing resistance, adhesion, hardness, high gloss, resilience, low thermal conductivity, ease of molding, ability to wet fillers, and oil resistance when cured. These compositions find use in phonograph records, protective coatings, adhesives, and electrical insulation.

Lignin Plastics.—Lignin plastics[2] are made from woody materials. Lignin is the binding material for the cellulose in live plants and in lignin plastics. The lignin bond of the woody material is released by the action of high-pressure steam which so activates the lignin that it can be used as a plastic binder. Wood chips are charged into suitable containers and treated with steam up to 1,200 lb. per sq. in. for a period of seconds. Normally the time cycle, including the filling and emptying of these containers, is about 1 min. In this time the lignin is softened by the sudden high temperature. When the chips are suddenly released to atmospheric pressure, they are exploded by the high internal pressure into a mass of fibers and fiber bundles which still contain the natural coating of lignin. These fibers are formed into mats under pressures from 50 to 300 lb. per sq. in. and at a temperature of about 180°C. The product is usually cured at a pressure of 1,500 lb. per sq. in. and a temperature of 175°C. The only plasticizer needed is about 4 per cent moisture which is present at the usual humidities. The curing is very rapid.

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[1] "Plastics Catalog," p. 168 (1943).

[2] "Plastics Catalog," pp. 190, 300 (1943), pictured flow sheet.

MANUFACTURE OF LAMINATES

Laminated plastics[1] are made largely from the thermosetting class of resins with fibrous fillers such as paper, cotton fabric, and asbestos. The resins and fillers may be consolidated by heat and pressure into dense, infusible, insoluble materials in the form of flat sheets, rods, angles, and piping. The resins are applied in the form of solutions in solvents such as alcohol or water. The phenol-formaldehyde type is dissolved in alcohol, and the urea-formaldehyde type is dissolved in water.

The resins are employed as varnishes with the fillers dipped or passed continuously through the solution so that all fibers are impregnated with resin and solvent. Gentle heat removes the solvent as the sheet is dried to the proper degree for partial polymerization to take place. The degree of drying is carefully controlled because too dry a material is brittle and an insufficiently dried material flows too readily during pressing.

Laminated products can be made in a variety of colors with or without printed designs and inlays. For plain effects a colored sheet is used with a backing. If designs or inlays are desired, the top sheet has the designs printed on with special urea inks. This printed sheet is dipped in the varnish solution and dried to the proper degree, and the various layers are consolidated under heat and pressure to form infusible, insoluble products. In making decorative inlays of metal or colored laminated plastics, the cut and designs are laid out on the surface of a sheet and pressed down into it to a point where they are level with the surface. The surface of a laminated sheet is determined by that of the steel press plate. For a glossy finish on the sheet the steel plate has a mirror surface. For a satin finish, the plate has a satin surface. Leather finishes or special raised designs are made with the use of carefully engraved plates.

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[1] Pictured flow sheet, *Chem. & Met. Eng.*, **47**, 183 (1940).

The laminated sheets should be cured and cooled in the mold. If the laminated sheets were removed from the mold while hot, the residual solvent in the varnish on the partly dried sheets would flash and cause blisters and surface irregularities. The curing time varies with the thickness of the material and its type. Urea laminates require about 2 hr. of curing time while the phenolic laminates require less time. The maximum temperature is about 270°F.

Decorative laminates[1] are harder than marble and will stand a great deal of wear. They are chemically inert and will not spot with fruit acids, alcohol or other solvents, or mild alkalies. The decorative laminates with the best and most stable colors are made with urea varnishes as pigment carriers. As the phenolic resins have a greater tendency to yellow with age, delicate colors cannot be used. Outstanding properties of decorative laminates are depth of color, durability, resistance to stains and cigarette burns, beauty of surface, chemical inertness, and resistance to discolorations.

Typical uses are for furniture tops, wall coverings, doors, elevator cab interiors, inlaid mural designs, telephone booths, counter tops and paneling, refrigerator door backs, translucent lighting fixtures, signs and displays, instruments and dials, translucent Venetian blinds, and architectural lights. Industrial laminates include gears, cams, bearings, rayon buckets, gaskets, coils, bushings, etc., where laminated plastics have several predominant characteristics that make them the ideal materials to be used. Such advantages are a high ratio of strength to weight, resilience or low modulus of elasticity, lightness in weight, resistance to corrosion, and low heat conductivity and machinability. These properties are permanent at normal humidities and temperatures.

Problem

Plastics as a whole are made of a very limited number of raw materials of which petroleum, lime, salt, coal, water, air, and naval stores are the most fundamental. Starting with those raw materials, prepare a chart showing all the intermediates involved in the manufacture of the following plastics: acrylate resins, vinyl resins, synthetic rubber (several types), phenolic resins, alkyd resins, and melamine resins.

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[1] "Plastics Catalog," p. 688 (1943).

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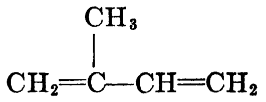
CHAPTER XXXVI

NATURAL AND SYNTHETIC RUBBER

Rubber is one of the most useful substances in the world today. Were it or allied substances removed entirely from our lives, technical civilization would be plunged into another Dark Age. The modern systems of communication and transportation would be greatly restricted and whole branches of business would disappear. Yet this product has not always been with us, for it was only about 100 years ago (1839) that the process of vulcanization was discovered, which made possible the successful manufacture and application of rubber.

In its real sense rubber is the product of the tree *Hevea brasiliensis* which originated in Brazil, whence it was transplanted to the Dutch East Indies, Ceylon, Burma, Liberia, and other places. A number of other plants yield rubbery products. Chemical evidence indicates that rubber is a natural polymerization product of isoprene:



$$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH{=}CH_2$$

The synthetic resilient materials are polymerized from different base chemical or chemicals and consequently are *not* rubber in the narrow conventional sense. However, these products are popularly called *synthetic* rubber. This chapter will be divided into two divisions: natural and synthetic rubber.

NATURAL RUBBER

Historical.—Rubber is one of the many useful products contributed to civilization through the discovery of America. Early historians recorded that Columbus on his second voyage saw the natives playing games with bouncing balls made from the juice of trees and that Emperor Montezuma in 1520 entertained Cortez and his soldiers with a game played with such balls. At an early date, the natives of southeastern Asia knew of rubber prepared from the juice of a tree. They had used it for a long time to make torches and to waterproof plaited baskets, jars, and other articles. It was from the New World, however, that Europeans received their first knowledge of rubber.[1]

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[1] Babcock, What Is Vulcanization? *Ind. Eng. Chem.*, **31**, 1196 (1939).

As early as 1736 two French scientists, Fresneau and la Condamine, made an effort to introduce rubber into Europe with little success. Joseph Priestley, English chemist and discoverer of oxygen, first called attention to the adaptability of rubber as a pencil eraser. This use was the source of the English name, *rubber.* Michael Faraday, another English chemist and physicist, determined the chemical composition of rubber, to which he assigned the formula $C_{10}H_{16}$, later superseded by $(C_5H_8)_x$.

The first commercial use of rubber was in 1791. Samuel Peal patented a process for making a waterproofed fabric by the treatment of cloth with a solution of rubber in turpentine. Rubber goods were not very satisfactory until after the advent of the vulcanization process. Warm summer weather caused them to become sticky, and cold winter weather caused them to become brittle. Many inventors endeavored to improve crude rubber or, as we now say, to vulcanize it. It was Charles Goodyear, however, who perfected the process of vulcanization and applied it to several hundreds of products through years of labor and experimentation.[1] Vulcanization is the process of combining rubber and sulfur under the influence of heat and pressure to change the rubber to an elastic, strong, nonplastic, and nontacky material.

In 1876, the British took 70,000 seeds of the *Hevea brasiliensis*, the chief rubber-producing tree, from Brazil to England and germinated them. The young plants were sent to Ceylon and Malay to be planted. This was the start of the huge rubber plantations which by 1910 produced more rubber than Brazil.[2]

Uses and Economics.—America consumed 663,000 tons of crude rubber in 1939 and over 740,000 tons in 1941.[3] The increase was due largely to the huge requirements of the Army and Navy. In normal times, such as 1939, the rubber is fabricated into 30,000 different articles. About 78 per cent is used in automobile tires, around 10 per cent in mechanical goods such as belting, molded goods, and packing, 3 per cent in boots, footwear, rubber heels, and soles, and 4 per cent in wire and cable insulation.[4] The remaining 5 per cent is employed in a myriad of familiar articles: waterproof clothing, floor mats, athletic equipment, and the like. It is interesting to note that the United States consumes about 50 per cent of the world's rubber production.[5]

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[1] BARKER and HOLT, "Rubber: History, Production and Manufacture," *U.S. Dept. Comm. Trade Promotion Series* 209 (1940).

[2] BABCOCK, *op. cit.*

[3] LONGSTRETH, Synthetic Rubbers, *Ind. Eng. Chem.*, **32,** 1156 (1940); HOLT, Present Status of Crude Rubber, *Ind. Eng. Chem.*, **33,** 1339 (1941).

[4] FINGER, Cooperation of the Rubber Industry with Defense, *Ind. Eng. Chem.*, **33,** 1335 (1941).

[5] BARKER and HOLT, *op. cit.*

Rubber was the item of greatest value imported by the United States during the period 1936–1940. Our annual bill for the product during this time averaged more than $151,000,000. It even exceeded such important commodities as cane sugar, coffee, wood pulp, and raw silk. About 500 American establishments are normally engaged in the manufacture of rubber products, and the industry gives employment directly to more than 150,000 persons who usually produce goods valued at over $1,000,000,000 annually at retail.[1]

MANUFACTURE

Rubber is a coherent, elastic solid obtained from a milky liquid known as *latex*, which, not to be confused with sap, occurs in a wide variety of tropical plants. The rubber is usually coagulated to remove the excess water in the latex before shipment to the consuming countries, where the vulcanization and fabrication take place.

Chemically, rubber, or coagulated latex, is a polymerized hydrocarbon, of which the structural unit is the isoprene radical. Various methods of determination of the molecular weight give values ranging from 10,000 to 435,000.[2] There is known to be one double bond for each C_5H_8 group. Though resistant to a great many chemicals, rubber is soluble in certain hydrocarbon solvents and in some of their derivatives, examples of both being pentane, benzene, chloroform, ether, carbon disulfide, gasoline, and lubricating oils. Ordinary crude rubber is insoluble in water but, with prolonged contact, it takes up large quantities of this substance. Rubber is practically incompressible, but its shape is easily changed under pressure. The practical importance of rubber is due to its physical properties, such as abrasion resistance, softness, toughness, elasticity, impermeability, adhesion, and electrical resistance. The instability of raw rubber to temperature conditions led to research for and the discovery of the vulcanization processes. The most characteristic property in the vulcanized state is that it can be stretched repeatedly to several times its length, and each time it returns to its first dimension. No other natural substance possesses this property.

Raw Materials.—The rubber of commerce is almost entirely the product of the tropical tree known as *Hevea brasiliensis*. The latex from this tree is a milky fluid which, without the addition of preservatives, soon becomes putrid and partly solidifies, *i.e.*, coagulates. Many other plants also produce latex, but latex-bearing plants of the cold and temperate zones are characterized by their small rubber content and only a few of those of the tropics contain sufficient quantities to warrant their commercial exploitation. On the whole, rubber is produced in a belt limited to 10° north and south of the equator.[1]

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[1] BARKER and HOLT, *op. cit.*

[2] MIDGLEY, Critical Examination of Some Concepts in Rubber Chemistry, *Ind. Eng. Chem.*, **34,** 891 (1942); KEMP and PETERS, Viscosity-molecular Weight of Rubber, *Ind. Eng. Chem.*, **33,** 1263 (1941).

The latex is obtained from the trees and sent to a plantation factory for treatment before shipment. It is diluted with water and the foreign matter allowed to settle. The diluted latex is coagulated with 1 per cent acetic acid whereupon the coagulum rises to the surface as a white, doughy material. This is milled to remove most of the moisture. Milled rubber may be smoked before shipment, or it may be milled very thin in creping machines and shipped as crepe sheets. Some products (rubber adhesives, rubber yarns and threads, surgical gloves, sponge rubber, etc.) require the use of uncoagulated latex. Caustic soda, formaldehyde, or ammonia, usually the latter, is added to the raw latex to prevent coagution during the period of transportation to the factory.

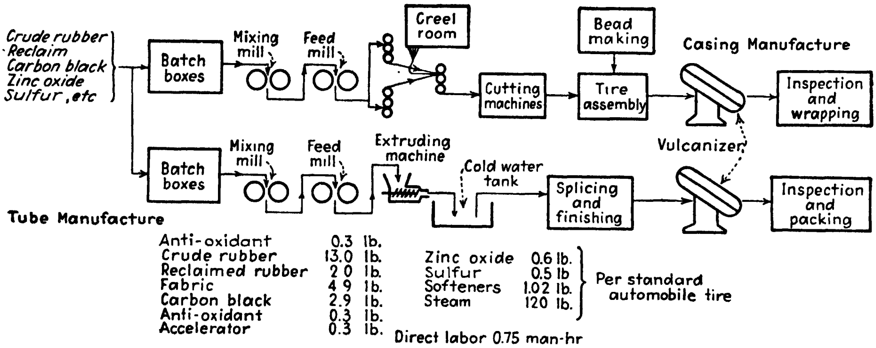

FIG. 1.—Flow sheet for rubber tubes and tires.

Manufacturing Procedures.—Rubber, in the natural state, is much too plastic and not sufficiently elastic to be very useful. Thus, essentially, the manufacture consists of vulcanization to impart elasticity and reduce plasticity. Other ingredients are added for various purposes: to prevent oxidation, to impart abrasion resistance, and the like.

Methods for manufacturing *rubber fabric articles* utilize appropriate sequences from the following procedures: (1) mastication of the rubber by mechanical action, (2) addition of compounding ingredients by further mechanical working, (3) sheeting out the rubber compound or extruding it in some special cross-sectional shape, (4) impregnation of fabric with rubber compound by calendering or by dipping of forms into rubber solution, (5) assembly of these unvulcanized materials into the approximate shape of the finished article, (6) vulcanization by means of heat and pressure or at room temperature in the presence of chemicals for a controlled and definite period of time.[1]

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[1] BARKER and HOLT, *op. cit.;* TRUMBULL, Growing Rubber in North America, *Ind. Eng. Chem.*, **34**, 1328 (1942).

The making of *automobile tires* illustrates the general principles of rubber manufacture. Figure 1 gives the essential features and may be divided into the following *unit operations* (Op.) and *unit processes* (Pr.):

The crude rubber is broken down in the masticating and mixing mill (Op.), which consists of two rolls revolving at different speeds and heated or cooled as desired. The rubber is softened, probably owing to the breaking up of long rubber molecules into shorter ones.[2] After the rubber is sufficiently milled, carbon black, zinc oxide, sulfur, reclaimed rubber, and softeners are added and the "compound" is milled sufficiently to incorporate all the materials (Op.). Each of the

TABLE 1.—TYPICAL FORMULAS FOR RUBBER ARTICLES[a]
(Parts by weight of ingredients used)

Item	Automobile tire tread	Automobile tire carcass	Black matting	Bathing cap	Bath sponge	Hard comb	Black boot upper	Black heel	Hospital sheeting
Rubber:									
Smoked sheets	100	75	12½	.....	...	100	100	67	
Crepe	.....	25	.....	100	100	...	.....	.....	100
Reclaimed rubber	.....	.....	175	.....	...	...	.....	67	
Vulcanizing agents:									
Sulfur	3	2¾	4½	1	3	45	2	3¼	¾
Others	.....	¾	.....	½	...	2	.....	.....	½
Accelerators	1	.....	1	1¼	1	...	1½	1	1¼
Accelerator-activators:									
Zinc oxide	3	5	2	2	5	...	5	3	5
Antioxidants	1¼	1	1	.....	2	...	¾	½	½
Rubber substitutes:									
Mineral rubber	.....	.....	50	.....	...	...	....	10	
Plasticizers:									
Stearic acid	4	1	.....	1	10	...	...	2	
Pine tar	1	1							
Others	1½	1	5	5	10	2	1	1	1
Odorants	.....	.....	.....	.....	...	...	.....	.....	⅒
Fillers and pigments:									
Carbon black	47	.....	.....	.....	...	...	30	17	
Clays	.....	15	160	.....	...	...	15	50	65
Others	....	.....	.....	10	25	...	30	.....	25
Other chemicals:									
Sodium bicarbonate	.....	.....	.....	.....	15				
Details of cure:									
Time, min	45	30	10	6	30	360	45	10	45
Temperature, °F	274	274	307	307	320	300	260	316	260
Steam, lb. per sq. in.	30	30	60	60	75	[b]	[c]	70	[c]

[a] R. T. Vanderbilt Co.; BARKER and HOLT, "Rubber: History, Production and Manufacture," *U.S. Dept. Comm. Trade Promotion Series*, 209 (1940).

[b] Between tinfoil in water.

[c] Dry heat cure; other cures by press.

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[1] BARKER and HOLT, *op. cit.*

[2] BUSSE, Mastication of Rubber, *Ind. Eng. Chem.*, **24**, 140 (1932).

ingredients added meets a definite purpose. The carbon black is a filler and serves to increase the abrasion resistance of the material. Zinc oxide is a vulcanization accelerator, sulfur is the vulcanizing material, and reclaimed rubber is used to lower the cost of the finished tire. Chemicals that act as vulcanization accelerators and antioxidants are incorporated to shorten the time of vulcanization and to protect the finished rubber from the aging action of air and light. Softeners or plasticizers are usually vegetable or mineral oils, waxes, and tars.

From the milling machines the rubber is run through calenders (Op.), which consist of three hollow rolls set one above the other. The rubber is forced into thin sheets, and cotton fabric (cords) is also introduced between the rolls so that the product is a thin sheet of rubber adhering to the fabric.

FIG. 2.—Milling or mixing rolls for compounding rubber before forming and vulcanization. (*Courtesy of The Goodyear Tire & Rubber Company.*)

The rubberized fabric is cut on the bias into strips (Op.). Thus the cords in the tire will be at an angle and give added strength.

The strips are formed over an iron core to produce the tire carcass. The tread, a heavy strip of masticated and compounded rubber, is shaped around the carcass and finally the bead is applied (Op.). The bead is a strip of very hard rubber containing wire threads embedded in it and forms the edge of the tire that is in contact with the rim of the wheel.

The assembled tire is placed in a mold into which the tread design has been cut. Heat, supplied by steam, and pressure for a very definitely controlled time cause the sulfur to vulcanize the rubber (Op. and Pr.).

The vulcanized tire is inspected and wrapped (Op.).

The manufacture of inner tubes is somewhat similar. The rubber is masticated and compounding ingredients added but, instead of being calendered into sheets, the rubber is forced through an extrusion machine. This is similar to a sausage machine and consists of a screw revolving in the bore of a cylinder which forces the rubber through a die to produce a tube of rubber. This tube is cut to the proper lengths, the ends of each piece are spliced to form a ring, inflated with air, and vulcanized with live steam in molds.

Although the fabrication and production of automobile tires and tubes are fairly representative of rubber manufacture, each article[1] made of rubber requires individual compounding formulas, ingredients, and handling. The successful compounding of rubber is complicated and varies greatly as Table 1 illustrates. The following list (by no means complete) of materials that are in general use gives some idea of the complexity of the rubber-compounding problem.

Vulcanizing agents: sulfur, selenium, tellurium, sulfur chloride, tetramethylthiuram disulfide (accelerator also).

Vulcanization accelerators: mercaptobenzothiazole, tetramethylthiuram disulfide, diphenylguanidine, acetaldehydeaniline (white lead).

Accelerator activators: stearic acid, lead monoxide.

Accelerator retarders: phenol, benzoic acid.

Antioxidants or age resistors: di-β-naphthyl-*p*-phenylenediamine, phenyl-α-naphthylamine, phenyl-β-naphthylamine, 4,4′-diaminodiphenylamine.

Plasticizers and softeners: vegetable and mineral oils, pine tar, rosin, zinc or lead soaps, and stearic acid.

Stiffeners: benzidine, *p*-aminophenol.

Reinforcing pigments: carbon black, certain clays, zinc oxide and blanc fixe.

Coloring pigments or fillers: ground barite, natural whitings, ferric oxide, antimony sulfide, lithopone, titanium oxide, ultramarine blue, organic lakes.

Rubber substitutes: factice (vegetable oils treated with sulfur or sulfur chloride), oils, bitumens.

Blowing agents: sodium or ammonium bicarbonate, diazoaminobenzene.

Vulcanization is one of the most important steps in the manufacturing process. It not only enhances the strength and elasticity of the rubber but markedly stabilizes the product.[2] The compounded rubber is placed in a mold or press, and pressure is applied. The heat is supplied by steam and may be either direct or indirect. Hot water is also employed or the fumes of sulfur chloride. The accurate control of time, temperature, and pressure is of the utmost importance.

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[1] PERRY, *op. cit.*, pp. 2162–2163, tabulates physical properties of rubber and lists representative makers of rubber products; pp. 920–921, presents data on hard rubber pipe and soft rubber-lined pipe.

[2] SHEPARD, A Century of Technical Progress in the Rubber Industry, *Ind. Eng. Chem.*, **25**, 35 (1933); GARNER, Vulcanizing Agents for Rubber, *Chem. Age* (London), **38**, 241 (1938); BABCOCK, What Is Vulcanization? *Ind. Eng. Chem.*, **31**, 1196 (1939); FISHER, Vulcanization of Rubber, *Ind. Eng. Chem.*, **31**, 1381 (1939).

Much work has been done on the theory of vulcanization, but as yet there has been no satisfactory explanation. Vulcanization is accompanied by the chemical combination of sulfur with the rubber hydrocarbon involving cross linkages. This reaction can be reversed. It is believed that this vulcanization reaction comes about through saturation of the double bonds or, according to a more modern theory, by cross linkages between methylene groups adjacent to the double bonds with sulfur or hydrogen sulfide taking part in the reaction.

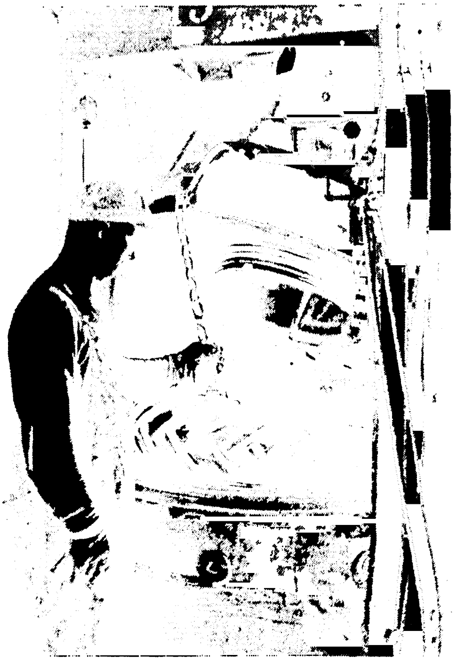

FIG. 3.—Removing a tractor tire from an individual machine after vulcanization. Note the instruments for the control of the process of vulcanizing by steam and pressure. (*Courtesy of The Goodyear Tire & Rubber Company.*)

Accelerators and Antioxidants.—The discovery of vulcanization accelerators and of antioxidants, or age resistors, has been a very important factor in decreasing the cost of rubber products and increasing their useful life. As Murrill[1] points out, the advantages arising from the use of vulcanization accelerators may be summarized, "Temperature of vulcanization was lowered, saving steam. Time of vulcanization was shortened, saving labor and equipment and increasing output. Quality of product was improved, giving greatly increased useful life."

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[1] MURRILL, Accelerators and Antioxidants in the Rubber Industry, *Chem. Eng. News*, **20**, 1361 (1942).

Light, heat, and the oxygen of the air have a deteriorating influence on rubber. The addition of certain chemicals (see Table 1) acts greatly to retard destruction of rubber in the conditions met with in normal usage. This increased service is nowhere better shown than in the doubling and tripling of the mileage obtained from automobile tires since the discovery and use of these compounds.

Energy Requirements.—As the mastication of rubber generates a large quantity of heat, the rolls of the compounding mill must be cooled to dissipate this heat. Energy must be supplied in the form of power to operate the mill and to run the calender and the extruding machines. Vulcanization requires external energy to supply both heat and pressure.

Latex.—Modern methods of partly concentrating and preserving liquid latex have opened new fields for rubber.[1] Rubber-coated fabrics and all types of sponge rubber and rubber threads are a few of the articles manufactured from latex. Compounding and vulcanization of latex are somewhat different from the same processes for sheet rubber.[2] The compounding and vulcanizing ingredients must be finely ground so that a uniform dispersion in the latex is possible. The latex may be vulcanized in either the liquid state or after coagulation. The usual procedure is to dip a glass form into the latex that contains the compounding and vulcanizing ingredients. The form is withdrawn; the rubber article is dried, vulcanized,[3] and stripped off. Sometimes the latex is subjected to a prior concentration.

Electrodeposition.—Articles may be coated with rubber by the action of an electric current. Liquid latex is subjected to an electrical action which liberates a positive charge. This positive charge neutralizes the negative charge of the rubber particles, and the particles coalesce.

The most fundamental and best known processes are the anode processes of which two have been developed: the anode electrodeposition on metals or on permeable material and the anode ionic deposition process.[4] In the first process a diaphragm cell is used for deposition on metals (see Fig. 4). The latex mixture is placed in the anode compartment, a zinc or iron anode is inserted, and slightly alkaline water is placed in the cathode compartment. A direct current is impressed on the electrodes, and the hydrogen and zinc ions react with the hydroxyl ions to neutralize the charge on the rubber particles which then coagulate and form a deposit on the anode.[1] Accurate pH control is necessary. Too low a pH causes soft deposits and too high a pH deposits with high electrical resistance. This type of deposition is particularly well suited for the application of coatings of soft and hard rubber to odd-shaped articles. If the rubber is to be deposited on permeable material, the anode is immersed in an electrolyte and the electrolyte is separated from the latex by permeable material. When an electric current is passed across the cell, a deposit of coagulated rubber forms on the diaphragm of permeable material.

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[1] Morris and Greenup, Rubber Latex, *Ind. Eng. Chem.*, **24**, 755 (1932): Hauser, Use of Latex in the Textile Industry, *Rayon Textile Monthly*, **18**, 617 (1937); Hauser, Latex and Its Uses, *India Rubber World*, **96**, No. 3, 42 (1937).

[2] Bradley, Vulcanization of Latex, *Ind. Eng. Chem.*, **31**, 1485 (1939).

[3] Hauser, Latex and Its Uses, *op. cit.*

[4] Sheppard, The Electrical Deposition of Rubber, *Trans. Am. Electrochem. Soc.*, **52**, 47 (1927); Beal, Anode Process for Rubber Articles and Coatings, *Ind. Eng. Chem.*, **25**, 609 (1933).

In the anode ionic deposition, the articles to be coated with rubber are covered with coagulating ions by dipping in a solution of polyvalent metallic salts, inorganic acids, organic acids, or any other desired latex coagulants. When such coagulant-coated surfaces are immersed in latex, the ions diffuse and coagulate deposits of latex rubber. This process is readily adaptable to the production of a wide variety of rubber articles on forms of metal, plastics, porcelain, and many other permeable or impermeable materials.[2]

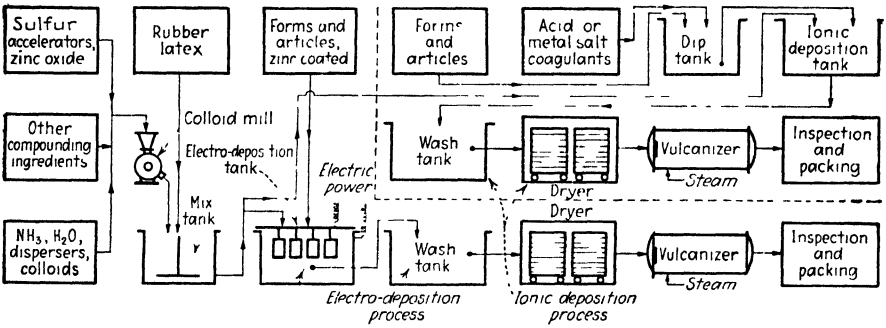

FIG. 4.—Flow sheet for anode process of rubber deposition.

Reclaimed Rubber.—Reclaimed rubber is prepared from discarded rubber products and rubber scraps. It is used in the manufacture of articles not requiring a high degree of elasticity. Rubber heels and soles, mechanical rubber goods, flooring, stoppers, and electrical insulation often consist (at least partly) of reclaimed rubber. Reclaimed rubber contains the crude rubber of the discarded rubber article after the reclaiming process has removed many of the compounding ingredients that were in the original mixture. The United States produced 170,000 tons of reclaimed rubber, valued at $17,000,000, in 1939.[3] This reclaim tonnage was greatly increased in 1942 and 1943.

The only successfully operated reclaiming processes are the alkali process and the acid process. The greater part of reclaimed rubber made from scrap that contains fabric is produced by the alkali process. It is significant that the reclamation of old rubber products is a highly technical undertaking that requires skilled workers, elaborate plant equipment, and large-scale operation for success.

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[1] PERRY, *op. cit.*, p. 2776, presents details for electrodeposition of rubber.

[2] BEAL, *op. cit.*; PERRY, *op. cit.*, p. 2777.

[3] "Reclaimed Rubber," 1939 Census of Manufactures, U.S. Department of Commerce, Bureau of the Census, 1940.

The scrap is prepared for reclaiming by chopping or grinding[1] it into small pieces. The small pieces are cooked in an autoclave[2] with a caustic soda solution at 340 to 370°F. The alkali removes the free sulfur in the scrap and also any fabric that may have been in or on the rubber. This treatment also restores some of the plastic properties to the rubber. The product is washed, dried, and is ready for fabrication (see Fig. 5 for further generalities).

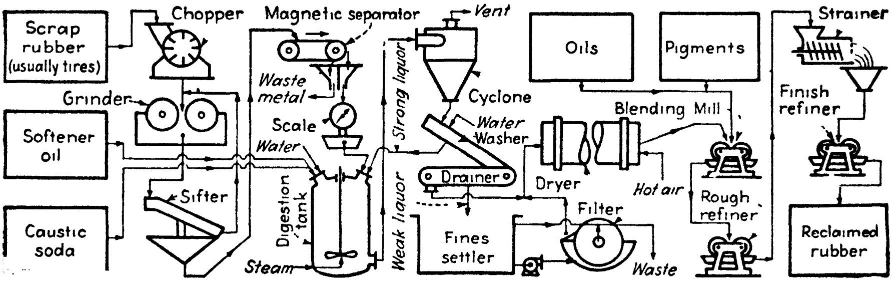

FIG. 5.—Rubber-reclaiming flow sheet.

The reclaiming of rubber originated during times of high rubber prices. However, in times of war it assumes a more important place as a means of supplying some rubber (albeit inferior) when no crude is available.

Chlorinated Rubber.—Chlorinated rubber is a white compound that possesses very little resemblance to rubber. It is prepared by treating a 4 per cent solution of rubber in carbon tetrachloride with chlorine.[3] The product contains 66 to 68 per cent chlorine. By varying the amount of chlorine in the product, materials of varying viscosities and thus varying uses can be prepared. *Pliofilm*, a transparent flexible sheeting containing 29 to 30 per cent chlorine, is prepared by adding hydrogen chloride rather than chlorine to rubber. Highly chlorinated rubber is useful as a waterproof, corrosion-resisting paint (*Tornesit*).

SYNTHETIC RUBBER

The development of synthetic rubber[4] has not followed the usual course of other synthetic chemical products. The customary procedure is analysis and determination of the structure of the natural product and then laboratory synthesis of an exact duplicate. Thus, a synthetic material is simply a man-made replica of a natural material. Synthetic rubber does not belong in this classification. Although the structure of rubber has been fairly definitely established, an exact duplicate has not yet been made. Some of the synthetic rubbers possess properties, such as oil resistance, that make these products superior to natural rubber for certain purposes.

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[1] PERRY, *op. cit.*, p. 1912, discusses the grinding of reclaimed rubber.

[2] SHEPARD, A Century of Technical Progress in the Rubber Industry, *op. cit.* A pictured flow sheet of the Akron reclaiming plant of the Goodyear Tire & Rubber Co. is presented in *Chem. & Met. Eng.*, **48,** No. 6, 112 (1941).

[3] LEE, How Rubber is Chlorinated, *Chem. & Met. Eng*, **46,** 456 (1939).

[4] The term *elastomer* has been suggested and seems to be gaining some favor as a substitute for the incorrect but popular term *synthetic rubber.*

Historical.—Prior to the First World War (1908–1914) Germany, Russia, and England carried out intensive research on synthetic rubber. This research was stimulated by two factors: the high cost of natural rubber ($2.07 a pound in 1910)[1] and the prospect of war with the resulting difficulties of obtaining crude rubber. All that developed from this intensive research program was the production of approximately 2,500 tons of methyl rubber (polymer of 2,3-dimethyl-1,3-butadiene) by Germany. The product was admittedly inferior to natural rubber and production stopped at the close of the war.[2]

Little, if any, research on this problem was conducted between 1919 and 1925. In 1925, the price of natural rubber rose sharply and efforts were made again throughout the world to synthesize a satisfactory rubber substitute. In the United States this research culminated in the production of chloroprene in 1931. About the same time Germany and Russia put on the market polymers of butadiene. Since 1931 many improvements have been made in these products and several others have been introduced.

Uses and Economics.—Many factors have influenced the development of synthetic rubber in various countries. The United States has endeavored to create products possessing special superior properties. On the other hand, Germany and Russia, impelled by the doctrine of "self-sufficiency," have bent their efforts to make products as nearly like rubber as possible at a reasonable cost.

The United States manufactured only 19,000 tons of synthetic rubber in 1941 and consumed in addition 740,000 tons of natural rubber.[3] This production, however, was a large increase over that of 1940 when only 4,500 tons were produced, but it still represented a very small fraction of our rubber needs. The production of synthetic rubbers in the United States is increasing greatly under the stimulus of the Second World War and is planned to be around 850,000 tons annually as summarized[1] in Table 3.

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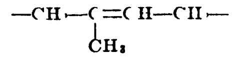
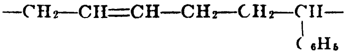
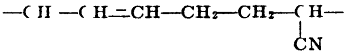
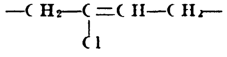
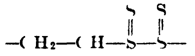
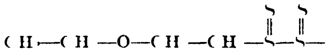
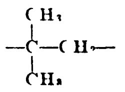
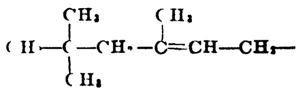
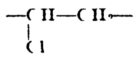
[1] BARKER and HOLT, *op. cit.* See SEMON, Thirty Years Contributions to the Science of Synthetic Rubber, *Chem. & Eng. News*, **21**, 1613 (1943).

[2] BRIDGWATER, Neoprene, the Chloroprene Rubber, *Ind. Eng. Chem.*, **32**, 1155 (1940).

[3] CRAMER, Industrial Progress in Synthetic Rubberlike Polymers, *Ind. Eng. Chem.*, **34**, 243 (1942).

The synthetic rubber made in the United States prior to the Second World War was for uses in which it was superior to natural rubber

TABLE 2.—CLASSIFICATION OF RUBBER AND RUBBERLIKE PRODUCTS

Raw materials	Polymer unit	Trade names
Latex from Hevea tree	 $-CH_2-\underset{CH_3}{\underset{\vert}{C}}=CH-CH_2-$	Rubber
Butadiene + styrene	 $-CH_2-CH=CH-CH_2-CH_2-\underset{C_6H_5}{\underset{\vert}{CH}}-$	Buna S GR S rubber (*U S Gov*) Chemigum S (*Goodyear*)
Butadiene + acrylonitrile	 $-CH_2-CH=CH-CH_2-CH_2-\underset{CN}{\underset{\vert}{CH}}-$	Buna N Perbunan (*Stanco Products*) Ameripol (*Goodrich and Phillips*) Hycar (*Goodrich and Phillips*) Chemigum N (*Goodyear*)
Chloroprene	 $-CH_2-\underset{Cl}{\underset{\vert}{C}}=CH-CH_2-$	Neoprene (*Du Pont*) Sovprene (*Russia*) Mustone (*Japan*) GR M (*U S Gov*)
Ethylene dichloride + sodium tetrasulfide	 $-CH_2-CH_2-\overset{S}{\overset{\Vert}{S}}-\overset{S}{\overset{\Vert}{S}}-$	Thiokol A (*Dow*) GR P (*U S Gov*)
Dichloroethyl ether + sodium tetrasulfide	 $-CH_2-CH_2-O-CH_2-CH_2-\overset{S}{\overset{\Vert}{S}}-\overset{S}{\overset{\Vert}{S}}-$	Thiokol B (*Dow*) Perduren (*Germany*)
Isobutylene	 $-\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}-CH_2-$	Vistanex (*Stand Oil of N J*) Oppanol (*I G Farbenindustrie*)
Isobutylene + isoprene	 $-CH_2-\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}-CH_2-\overset{CH_3}{\overset{\vert}{C}}=CH-CH_2-$	Butyl (*Stand Oil of N J*) Flexon (*Stand Oil of N J*) GR I (*U S Gov*)
Vinyl chloride + plasticizer	 $-\underset{Cl}{\underset{\vert}{CH}}-CH_2-$	Koroseal (*Goodrich*) Korogel (*Goodrich*) Flamenol (*General Electric*)

NOTE. In case of the copolymers the polymer unit as given above is only approximate as it is usual to have a smaller amount of the second constituent than the molecular equivalent structurally depicted above. Furthermore the individual products sold under the trade names Ameripol, Hycar have not had their structure definitely announced. Under one of the Thiokol varieties is the polymer from the condensation product of sodium polysulfide and dichloro-ethyl formal; this synthetic rubber is not troubled by the heating caused by hysteresis.

Now that the necessity has arisen to produce synthetics to replace natural rubber, the questions of special uses, higher prices, and the like are not of so much importance as the ability to manufacture quickly a more or less satisfactory product for tires.

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[1] KIRKPATRICK, American Rubber (Chemical Engineering Award), *Chem. & Met Eng*, **50**, No. 11, 100 (1943), entire synthetic rubber project with breakdown of $650,000,000 investment.

The cost of synthetic rubbers in August, 1941, ranged from 45 to 75 cents a pound, compared to 23 cents for the natural material.[1] However, large-scale manufacture has lowered the cost considerably.

Classification of Synthetic Rubbers.—Some of the rubberlike products are related chemically to natural rubber; others have only a physical relationship. Although rubber is made up of isoprene units, none of the commercial synthetics utilizes isoprene as a starting material. Instead, the most common raw material is the closely related 1,3-butadiene. Table 2 gives some of the more important types[2] of synthetic rubbers with their polymer building units.

MANUFACTURE

The manufacture of synthetic rubbers has involved two problems: the economical production of the raw materials and the actual polymerization. As the direct raw materials for the polymerization have not heretofore been available in the tonnages required, special plants have been designed and installed. The basic materials for all the synthetics are farm-grown carbohydrates, coal, crude petroleum, limestone, salt, water, and air.

The United States has embarked on a very essential and far-reaching program for synthetic rubber manufacture. This, as summarized in Table 3, represents the rated capacities[3] at the end of 1943.

Raw Materials.—*Butadiene*[4] is produced chiefly from petroleum gases. The thermal processes of cracking petroleum can be modified to give appreciable yields of butadiene largely by increasing temperature and lowering pressure. But more than half of the 700,000 tons of butadiene eventually needed per year will be produced by the catalytic dehydrogenation of butane or of butene (butylene). If butane is employed, it is first dehydrogenated to butene and then to butadiene.

$$C_4H_{10} \rightarrow C_4H_8 + H_2; \qquad C_4H_8 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + H_2$$

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[1] CRAMER, *op. cit.*

[2] HOLLIMAN, A Directory of Synthetic Rubbers, *U.S. Bur. Mines Circ.* 7242, May, 1943; published in condensed form, *Chem. Industries*, **53**, 63 (1943), lengthy bibliography; FISHER, Coal in the Manufacture of Synthetic Rubber, *Ind. Eng. Chem.*, **34**, 1382 (1942).

[3] DEWEY, The Rubber Program, Present and Future, *Chem. Eng. News.*, **21**, 1503 (1943).

[4] FROLICH and MORRELL, Butadiene, *Chem. Eng. News*, **21**, 1138 (1943), excellent survey with many references; NORTH, Rubber from Petroleum Gases, *Chem. & Met. Eng.*, **47**, 220 (1940); EGLOFF and HULLA, Production of Butadiene, *Chem. Industry*, **51**, 719 (1942); ELDER, Progress of Butadiene Production, *Ind. Eng. Chem.*, **34**, 1260 (1940); ANON., Butadiene from Petroleum, *Chem. & Met. Eng.*, **50**, No. 7, 104 (1943); RAIGORODSKY and DOTTERWEICH, War Products from Natural Gas and Natural Gasoline, *Petroleum Refiner*, **22**, 125 (1943), charts and processes; ANON., Port Neches Butadiene Plant Now on Stream, *Petroleum Refiner*, **213**, No. 3, 83 (1944).

TABLE 3.—UNITED STATES SYNTHETIC RUBBER PROGRAM, 1943
(Annual rated capacities, by type and feed stock)

	Long tons	Percentage
Buna S:		
From butenes.	317,000	[illegible].3
From butane	82,000	9.6
From thermal cracking.	83,000	9.8
From alcohol	253,000	2 8
Butyl:		
From isobutylene	75,000	8 8
Neoprene:		
From calcium carbide.	40,000	4 7
Total	850,000	100 0

The material obtained from any of the petroleum processes is not pure enough to be used for polymerization and must be purified. The boiling point of butadiene is −4.5°C. and that of 1-butene, for example, is −6.2°C., while isobutylene has a boiling point of −6.7°C. A withdrawing agent that forms a constant boiling mixture with butadiene has been employed that so depresses the volatility of the butadiene that the olefins are boiled off in advance. This procedure enables the commercial production of 99 per cent butadiene.

Another procedure for separating butadiene from the accompanying hydrocarbons depends on the formation of intermediate chemical compounds of varying stability. Copper, mercury, or silver salts will give such compounds with olefins, diolefins, and acetylenes, but not with paraffinic hydrocarbons. As Frolich and Morrell state, "By taking advantage of the relative stabilities of these addition compounds, it is possible to regenerate selectively the butadiene in a highly concentrated form."

However, solvent extraction, somewhat similar to that employed for the refining of petroleum lubricating oils, seems to be the best method for purification of butadiene from petroleum.[1] A solvent that has found favor for this difficult separation of closely boiling products is furfural.

Several processes are available for the production of butadiene from ethyl alcohol[2] or farm products. The Lebedev (Russian) method consists of catalytically converting two moles of ethyl alcohol to one mole of butadiene.

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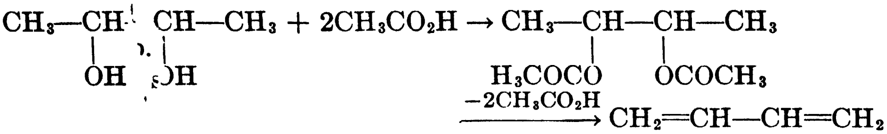
[1] FITZGERALD, New Uses for Solvent Processes, *Petroleum Refiner*, **22**, No. 10, 317 (1943).

[2] GAMMA and INOUYE, Manufacture of Butadiene from Ethyl Alcohol, *Chem. & Met. Eng.*, **49**, No. 12, 97 (1942); **50**, No. 1, 94 (1943), reactions, flow charts, and references.

$$2C_2H_5OH \xrightarrow{\text{Catalyst}} CH_2{=}CH{-}CH{=}CH_2 + 2H_2O$$

A new method consists of fermenting grain to 2,3-butylene glycol. Acetylation and subsequent deacetylation give good yields of butadiene.



$$\underset{\substack{|\\OH}}{CH_3{-}CH}{-}\underset{\substack{|\\OH}}{CH}{-}CH_3 + 2CH_3CO_2H \rightarrow CH_3{-}\underset{\substack{|\\H_3COCO}}{CH}{-}\underset{\substack{|\\OCOCH_3}}{CH}{-}CH_3 \xrightarrow{-2CH_3CO_2H} CH_2{=}CH{-}CH{=}CH_2$$

A European process uses acetaldehyde (which may be prepared from either acetylene or ethyl alcohol) as the raw material.

$$\underset{\text{Acetaldehyde}}{2CH_3CHO} \rightarrow \underset{\text{Aldol}}{CH_3CH(OH)CH_2CHO} \xrightarrow{+H_2}$$
$$\underset{\text{1,3-Butylene glycol}}{CH_3CH(OH)CH_2CH_2OH} \xrightarrow{-H_2O} \underset{\text{Butadiene}}{CH_2{=}CH{-}CH{=}CH_2}$$

Although this process is long, it is reported to give good yields of a very pure product.[1]

The process employed in the 80,000-ton butadiene plant[2] operated by the Carbide and Carbon Chemicals Corp., at Institute, W. Va., makes the butadiene from ethyl alcohol. The alcohol is catalytically oxidized to acetaldehyde which is reacted hot with more alcohol in the presence of a catalyst to form the butadiene. The reactions may be presented as follows:

$$\underset{\text{Alcohol}}{C_2H_5OH} + \text{air} \xrightarrow{\text{Catalyst}} \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2O$$
$$\underset{\text{Acetaldehyde}}{CH_3CHO} + \underset{\text{Alcohol}}{C_2H_5OH} \xrightarrow{\text{Catalyst}} \underset{\text{Butadiene}}{CH_2{=}CH{-}CH{=}CH_2} + 2H_2O$$

It is probable that the acetaldehyde and alcohol combine to form 1,3-butylene glycol which loses water to give the butadiene. The reaction product is cooled in heat exchangers and condensers to furnish a crude butadiene, which is rectified by distillation from the uncracked raw materials, resulting in a 98.5 per cent pure butadiene.

Chloroprene, 2-chloro-1,3-butadiene, is made by treating vinylacetylene with cold, aqueous hydrochloric acid. The essential steps starting with acetylene are

$$2HC{\equiv}CH \xrightarrow{\text{catalyst}} \underset{\text{Vinyl-acetylene}}{CH_2{=}CH{-}C{\equiv}CH} \xrightarrow[Cu_2Cl_2\ +NH_4Cl]{+HCl} \underset{\text{Chloroprene}}{CH_2{=}CH{-}CCl{=}CH_2}$$

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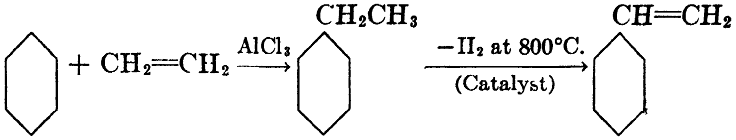
[1] Wood, "Synthetic Rubbers," *Nat. Bur. Standards Circ.* C427, Washington, 1940.

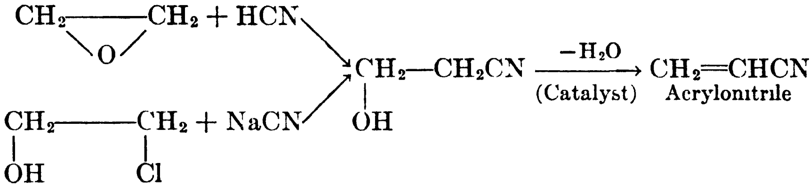
[2] Lee, GR-S Rubber, *Chem. & Met. Eng.*, **50**, No. 6, 98 (1943); a pictured flow sheet is also given, on pp. 140–143.

Styrene, vinyl-benzene, is prepared starting from benzene and ethylene by a Friedel-Crafts reaction. This is dehydrogenated by mixing with steam at 800°C. in the presence of a bauxite catalyst.



The first product is ethyl-benzene which is catalytically dehydrogenated to yield styrene.[1] Production in 1943 was around 350,000,000 lb.

Acrylonitrile is made by the dehydration of ethylene cyanohydrin, which may be prepared by adding hydrogen cyanide to ethylene oxide or by treating ethylene chlorohydrin with sodium cyanide.



Isobutylene is obtained from petroleum (Chap. XXXVII). The chloro-compounds used for the production of Thiokols are well-known chemicals. See Figs. 18 and 20, Chap. XXXVII, for source of isobutylene and butadiene from the products of the petroleum industry.

Polymerization.—The synthetic rubbers made from butadiene and chloroprene are true polymers; *i.e.*, the final molecule is composed of many small molecules added together and with none of the original atoms of the monomer eliminated in the process. Products of the Buna S and Buna N type are *copolymers* from two raw materials. The polysulfide rubbers are, however, *condensation polymers.* The chlorine of the hydrocarbon and the sodium of the tetrasulfide do not appear in the polymer (see Table 2).

Polymerization of the butadiene type may be carried out by one of two methods: bulk and emulsion.[2] The bulk method consists of combining the monomers with a suitable catalyst (such as sodium) and with or without a diluent. This method has been almost entirely replaced by the emulsion method. Emulsion polymerization involves emulsion of the monomers in a liquid, usually water and soap, before catalytic polymerization by heat. After polymerization, the product resembles latex and can be coagulated with dilute acids.

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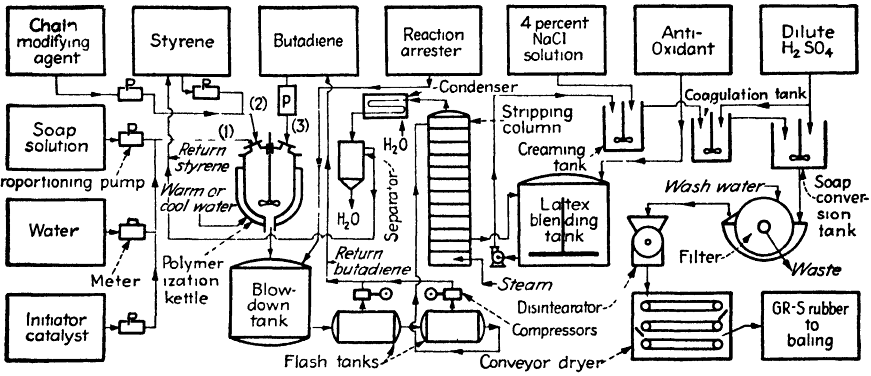
[1] Dow, Progress in Styrene Production, *Ind. Eng. Chem.*, **34**, 1267 (1942); *Chem. & Met. Eng.*, **51**, No. 2, 159 (1944), pictured flow sheet.

[2] Naunton, "Synthetic Rubber," Macmillan & Company Ltd., London, 1937.

The preparation of *Buna S* is typical of the butadiene types of synthetic rubber[1] and is presented in Fig. 6, which illustrates the main steps with the quantities of the principal raw materials. This flow sheet may be broken down into the following coordinated sequences of *unit operations* (Op.) and *unit processes* (Pr.):

The soap solution is diluted with water at a slightly elevated temperature in a wooden vat, to which the initiating catalyst is added (Op.).



	Per year		Per Year
Butadiene	80 000 tons	Chlorine	46 tons
Styrene	25,000 tons	Alum	345 tons
Soap (Sod. stearate)	4,500 tons	Soda ash	127 tons
Rock salt	20 000 tons	Sod metaphosphate	13 tons
Water	173,000,000 gal *	Also unstated quantities of H_2SO_4, NaOH, initiator catalyst, chain modifier, reaction arrestor, anti-oxidant	
Coal	1,100 tons*		

* Per day

Water treatment

For manufacture of 100,000 tons per year of Buna S rubber (Based on the plant at Institute, W Va

FIG. 6.—Manufacture of synthetic rubber, Buna S or GR-S – based on the plant at Institute, W. Va. The capital expenditure is 56 million dollars and the operating personnel is 1,500 men and women. Tons given above refer to short tons.

The preceding mixture is passed into a 2,500-gal., glass-lined (or stainless-steel) autoclave (Op.).

The styrene containing the chain modifying agent is pumped into the autoclave (Op.).

The stirrer of the autoclave is started and the air evacuated, excessive frothing being guarded against (Op.).

The required amount (about 75 parts for 25 parts of styrene) of butadiene is now pumped into the autoclave (Op.).

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[1] See *Chem. & Met. Eng.*, **49**, No. 6, 76 (1942) for simplified flow sheets for butyl rubber and Neoprene; ANON., Production of Buna-S Synthetic Rubber, *Chem. & Met. Eng.*, **50**, No. 6, 140–143, 98–102 (1943), pictured flow sheet of 90,000-long-tons-a-year plant at Institute, W. Va.; BROTHMAN and WEBER, Batch-continuous Process for Buna S, *Chem. & Met. Eng.*, **50**, No. 3, 108 (1943); MURPHY, The U.S. Synthetic Rubber Program Moves Forward, *Chem. Eng. News*, **21**, 864 (1943), description of the plant at Institute, W. Va. For flow sheet and pictures of the petroleum butadiene Buna-S rubber plant at Baton Rouge, see Van Antwerpen, Molecular Magic, *Chem. Eng. News*, **21**, 955, 986 (1943).

Copolymerization is carried on under controlled conditions, the temperature being maintained at 52°C. for 15 to 20 hr. (Pr.); this requires mild heating with hot water at the start following by cooling, as the reaction is exothermic (Op.); the pressure, owing largely to the butadiene, is at 60 lb. per sq. in. at the start and drops to 35 lb. in 12 to 18 hr. when the reaction is about 75 per cent completed. (Partial copolymerization produces better rubber than a complete reaction.)

FIG. 7.—A step in the manufacture of Neoprene—the plastic polymer being poured from a kettle. (*Courtesy of E. I. du Pont de Nemours & Company, Inc.*)

The copolymerization mass with the excess of reactants is run under its own pressure to a blowdown tank where a reaction arrester is introduced (Op.).

The excess butadiene is recovered for reuse by passing the reaction product through first a flash still at 3 lb. per sq. in. pressure and second a vacuum still (Op.).

The excess styrene is removed in a steam stripping bubble-cap still (Op.).

Many batches of latex are blended in large concrete tanks, an antioxidant being added by a proportioning pump as the latex enters (Op.).

The Buna-S latex is creamed in a wooden tank with a 4 per cent salt solution containing a little alkali and some glue, resulting in a flocculation of the rubber particles (Op.). The latex is coagulated and the soap converted to fatty acid by action of dilute sulfuric acid (Pr.) employing Monel metal pumps and fittings to lessen corrosion.

The rubber floc is filtered and washed on rotary Oliver filters (Op.).

The rubber crumbs are conveyed to a disintegrator, then dried continuously; finally, the Buna-S rubber is compressed into 75-lb. blocks and baled for shipment (Op.).

Neoprene.—The reactions by which this first of the successful synthetic rubbers is made are as follows:

$$\underset{\text{Acetylene}}{2CH\equiv CH} \xrightarrow[\text{alyst}]{\text{Cat-}} \underset{\text{Vinyl-acetylene}}{CH\equiv C{-}CH{=}CH_2} \xrightarrow{HCl} \underset{\text{Chloroprene}}{CH_2{=}CCl{-}CH{=}CH_2}$$

$$\underset{\text{Chloroprene}}{nCH_2{=}CCl{-}CH{=}CH_2} \text{ polymerizes to } \underset{\text{Neoprene}}{({-}CH_2{-}CCl{=}CH{-}CH_2{-})_n}$$

These reactions require exact control to carry out successfully on a manufacturing scale,[1] as compounds are being handled that can decompose with violence. Certain amounts of acetylene and of divinyl-acetylene are distilled in the course of the making of the vinyl-acetylene. The divinyl-acetylene goes to the synthetic drying oil plant (S.D.O.).

Butyl Rubber.—This has proved to be one of the most difficult of the synthetic rubbers to fabricate on a large scale. It has excellent properties of chemical inertness and low permeability to gases that make it desirable in special applications. It is copolymerized[2] from isobutylene and isoprene (Table 2).

Thiokol.—The condensation of ethylene dichloride and sodium tetrasulfide and the subsequent polymerization are somewhat different.[3] A sodium tetrasulfide solution is added slowly to the ethylene dichloride. Magnesium hydroxide is introduced into the polysulfide solution as a dispersing agent. The temperature is held at 80°C., and the mixture is agitated vigorously for 5 hr. This produces a latex in which the solid material gradually settles out. The excess water is decanted, the solid material is washed several times with water, and finally hydrochloric acid is added to coagulate the rubber. The rubber forms in a thick sheet at the bottom of the vessel. After removal of the solution, workmen cut out the rubber from the vessel. The product is then dried and shredded and is ready for mastication.

Mastication, Compounding, and Vulcanization of Synthetic Rubber.—Although carried out on the same equipment as natural rubber, the compounding of synthetic rubber presents many new problems. Few, if any, of the synthetics mill as satisfactorily as rubber, and special techniques have been devised for each case. For example, the milling of the butadiene-acrylonitrile copolymer is very difficult and develops much more heat than natural rubber. On the other hand chloroprene polymers mill quite readily.[1]

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[1] *Chem. & Met. Eng.*, **51,** No. 1, 130 (1944), pictured flow sheet.

[2] LEE, *Chem. & Met. Eng.*, **50,** No. 7, 102, 132 (1943) pictured flow chart; POWERS, "Synthetic Resins and Rubbers," pp. 222–230, John Wiley & Sons, Inc., New York, 1943.

[3] HARRAGAN, Manufacture of Thiokol, *India Rubber World*, **95,** No. 3, 38 (1936).

Faced with the problem of producing synthetic rubber for general uses and not for specialty articles, the United States will doubtless improve the present synthetics and their compounding in the next few years, particularly since many people are employed in research on this subject. It is too early to evaluate these synthetic resilient products, as to both competitive cost and competitive properties, although in the Second World War synthetic rubbers have been of fundamental importance and have relieved a national emergency.

Buna-S type resembles natural rubber most closely and is employed chiefly for the fabrication of tires that approach those from natural rubber in their road wear.

Other synthetics have specific properties that make them superior in certain fields. The first commercial example of this is neoprene, the oil resistance of which in prewar years enabled it to sell at several times the price of natural rubber for hose to transport oil and gasoline, or for gasket material. Neoprene also possesses superior resistance to flame or degrading influences of sunlight and air, caused probably by the chlorine content of the neoprene.

On the other hand, butyl[2] rubber (as well as other isobutylene products) is quite soluble in petroleum hydrocarbons but, because of their almost complete lack of unsaturation, these are chemically very resistant to attack by acid, alkalies, and ozone. Their vulcanizates are highly impermeable to gases and are being proposed for inner tubes.

Another example of a specific application is the use of Thiokol FA[3] to line concrete tanks employed for gasoline and oil storage. The Thiokol is not attacked by the petroleum products and thus prevents loss, but also it protects aviation gasoline from the drop in octane rating that the alkali of the concrete would bring about.

Problems

1. Certain ingredients are generally added to rubber in very small quantities. To aid in the rapid incorporation of these materials and in the accuracy of the measured quantity used, the chemical to be added is often blended into a "master batch" of rubber separately, and small known weights of the master batch are added to the rubber as it is worked on the rolls. A certain rubber formula is to contain, among other things, in the finished product 0.56 per cent Captax, 0.49 per cent phenyl-β-naphthylamine, and 65 per cent smoked sheet, the entire batch weighing 150 lb. The chemist uses 100 lb. of smoked sheet to make up a master batch of Captax containing 5 per cent Captax. Later, by error, he incorporates 6 lb. of phenyl-β-naphthylamine into this batch. In order to avoid discarding the master batch, he adjusts its components to a fixed ratio between Captax and phenyl-β-naphthylamine. What will be the composition of the master batch and how much master batch should be added to the batch on the mill to give the proper proportions of Captax and phenyl-β-naphthylamine in the finished product?

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[1] STARKWEATHER and YOUKER, Plasticization of Neoprene G, *Ind. Eng. Chem.*, **31**, 934 (1939); MOLL, HOWLETT, and BUCKLEY, Perbunan Properties and Compounding, *Ind. Eng. Chem.*, **34**, 1284 (1942). For an excellent study of properties of synthetic rubber, see Sebrell, The Second Mile, *Ind. Eng. Chem.*, **35**, 730 (1943).

[2] HAWORTH and BALDWIN, Butyl Rubber Properties and Compounding, *Ind. Eng. Chem.*, **34**, 1301 (1942).

[3] ANON., Synthetic Rubber Linings for Concrete Fuel Storage Tanks, *Chem. Eng. News*, **21**, 579 (1943).

2. Butyl rubber is polymerized at an extremely low temperature, frequently as low as −100°F. At these temperatures extreme care should be taken to provide absolutely dry ingredients to avoid formation of ice on the heat-transfer surfaces and to avoid the loss of heat. After polymerization the charge must be heated to +150°F. Describe the precautions necessary to make this process feasible from the standpoint of heat consumption and freedom from icing troubles.

3. Tennis balls are made by curing two halves around a pill of ammonium nitrite, then decomposing the nitrite by heat to inflate the interior.

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

If the ball is a 2-in. diameter sphere, how much ammonium nitrite must be added to give an internal pressure of 50 lb. per sq. in. gage at 70°F. after it is decomposed according to the above formula? Assume the ball to be at a temperature of 30°C. at the time the pill is inserted.

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CHAPTER XXXVII

THE PETROLEUM INDUSTRY

America is indeed fortunate in her petroleum situation. She stands at the head of other nations in her resources of crude petroleum, in her transportation of petroleum products, and in her refineries for processing crude petroleum into products of greater usefulness. If we except the primary production of food and clothing from our soils, there is no organic industry more important to modern technical civilization than the petroleum industry.

Initially, the refining of petroleum involved the simple separation of the constituents already present in the crude oil. This was the easiest approach, and it was lucky that the first crude oil discovered in Pennsylvania was adapted to such an operation. However, as markets were developed for more specialized products and as new fields supplying crude oil were discovered, it was necessary to apply chemical treatment to the refining of simple petroleum products. It also became economical to use chemical reactions to change the molecular structure of the compounds initially present in the crude, thus opening up greatly enlarged and more adaptable markets to the petroleum industry. *During the past 20 years the conviction has been gaining ground that the petroleum industry offers the cheapest and one of the most important sources of raw materials for the production of a great variety of the chemicals that enter into various phases of our present complicated industrial life.* Although the petroleum industry faces the prospect of importing more and more crude oil, it is not at all likely that the use of petroleum products as chemical raw materials will be curtailed.[1] Rather, the consumption of petroleum products as fuels may become relatively less and less as the decades go on and it is more economical to process coal and its products.

The petroleum industry in its design, operation, development, sales, and executive branches has become the largest employer of chemical engineers. This has been particularly true recently because the simple distillations of the earlier years have been generally replaced by complicated refining procedures which involve numerous unit operations and unit processes, frequently of great complexity and large size. This

[1] BROOKS, A New Phase of the Petroleum Industry, *Chem. Eng. News*, **21,** 939 (1943); reserves and trends in the petroleum industry are carefully discussed. FROLICH, Petroleum, Past, Present, Future, *Ind. Eng. Chem.*, **35,** 1131 (1943), an excellent general survey with many tables, including a gasoline cost tabulation.

industry is so interrelated and so technical in all its branches that the trained engineer is a necessity. He should not become too narrow in his view as the petroleum industry is reaching out into many other chemical fields, supplying raw materials, or using other chemicals. Thus chemical engineers within the petroleum industry should know something of other fields to be most efficient whether in operating, constructing, or designing work.

Historical.—It seems hardly believable that the petroleum industry has grown so rapidly and so extensively from the first skimming of petroleum seepages by the Indians for a medicinal or rubbing oil or the first petroleum well drilled near Titusville, Pa., by Colonel Drake in 1859 to the tremendous industry now flourishing, not only in the United States but throughout the world. This development has gone through a great many changes as markets have developed. At first, the chief petroleum product sold was kerosene for illuminating purposes. Now kerosene is of secondary importance in comparison with the tremendous consumption of gasoline occasioned by the growth of the internal-combustion engine and its application to transportation or to power, in the air, on our roads, in our factories, and on our farms. Recently we have seen the synthesis of many other chemicals out of petroleum products.

Chemical engineering owes a great deal to the discovery and application of engineering principles in distillation, heat transfer, fluid flow, and the like by the petroleum engineers in the designing, building, and operating of their refineries. At first their almost universally used equipment was a batch still. Here a relatively small amount, or batch, of crude petroleum was pumped into a horizontal direct-fired cylindrical vessel provided with a condenser. The various constituents of the petroleum were distilled and condensed, the lightest coming over first and leaving behind in the still a residuum of tar or heavy lubricating oil. This has been supplanted almost entirely by the modern *continuous* still, as will be exemplified by the flow sheets presented in this chapter.

Origin.—There is much dispute as to the origin[1] of petroleum, there being both inorganic and organic theories. One of the chief inorganic theories is that petroleum arose from polymerization and other reactions of such materials as acetylene, resulting from the action of water upon metallic carbides. There are, however, very few such carbides present in nature, and it is difficult to conceive of their formation in the quantities necessary and in relation to the rocks with which petroleum is associated.

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[1] *Cf.* ILLING, LIND, TRASK, BROOKS, and HOBSON in DUNSTAN, NASH, BROOKS, and TIZARD, "Science of Petroleum," Vol. 1, pp. 32–56, Oxford University Press, New York, 1938. This large four-volume publication on petroleum is a monumental work and should be freely consulted by anyone interested in petroleum.

Present opinion has moved away from the notion of an inorganic to an organic origin.

There have been many organic theories of the origin of petroleum, some emphasizing a vegetable or animal background, others a close relationship to coal, while certain of these theories lay stress on how any organic matter of either background could be transformed into petroleum products. There seems to be general agreement that petroleum has been formed from organic matter of marine nature, associated with the sediments later on solidified into the rocks: limestones, dolomites, shales, or sandstones. The concentration of the organic matter may not have been high in the original deposition, but petroleum has migrated and gathered in places most favorable to its retention, such as porous sandstone in domes protected by oil-impervious strata or against sealed faults in the sediments. Brooks concludes[1] that petroleums are not equilibrium mixtures, that their wide differences in composition probably relate to differences in original source material, and that "fatty oils are still to be regarded as the principal source material of petroleums." He favors a low temperature, 140°F., for the formation of petroleum, following an anaerobic "putrefactive decomposition of the organic matter deposited in the sediments," wherein the fatty acids lose carbon dioxide.

Exploration.—At one time the drilling for petroleum was a hit-or-miss affair and in such cases about 1 out of 300 of the "wildcat"[2] wells struck oil. However, by employing skilled geologists who have studied the origin and occurrence of petroleum, as well as geophysicists, who are expert in the use of very delicate instruments to determine something about the geological conditions under the earth's surface, the drilling of wells has become almost an exact science, so that now about 78 per cent of the new wells yield oil or gas. The geologist early recognized that petroleum occurred in oil pools caught in the anticlinal folds of sedimentary rocks. The success of the oil geologist[3] has been due to the correlation of a great deal of experience and data. This includes the study of cores from all types of wells and the accurate observation of surface indication, coupled with newer geophysical exploratory procedures, many of which have been developed and perfected by the scientific staffs of the oil companies.

By the use of very sensitive instruments, the geophysicists can determine the likelihood of the occurrence of domes and deposits at considerable distances in the earth. The top of the arch of an anticline, or a dome, has, by virtue of compression, a greater specific gravity than the surrounding rocks, as shown by Fig. 1, which depicts the various strata surrounding oil-bearing rock or sand. Oil and salt deposits also have a different (lower) specific gravity than the accompanying rocks. These variations are measured by very delicate gravity instruments which record changes in the gravity constant *g*. The plotting of these results gives us a *gravimetric survey*. Other methods of forecasting such anticlines include the exploding of dynamite charges at stated intervals with special instruments located at various points to measure and time the reflected wave initiated by the explosion. This results in a *seismic survey*. Other methods are also used, such as a determination of the electrical conductivity of the earth or the magnetic conditions. These two methods do not seem to be so successful as the gravimetric and seismic surveys. All these studies lead to the drilling of a test well which, if successful, frequently opens up a new oil field.

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[1] "Science of Petroleum," Vol. 1, p. 52.

[2] A "wildcat" is a well whose location is determined without resorting to scientific exploration of any kind, especially in a previously untested area.

[3] See "Science of Petroleum," particularly pp. 270–397, for numerous articles by experts in this field. See also, HAGER, "Practical Oil Geology," 5th ed., McGraw-Hill Book Company, Inc., New York, 1938.

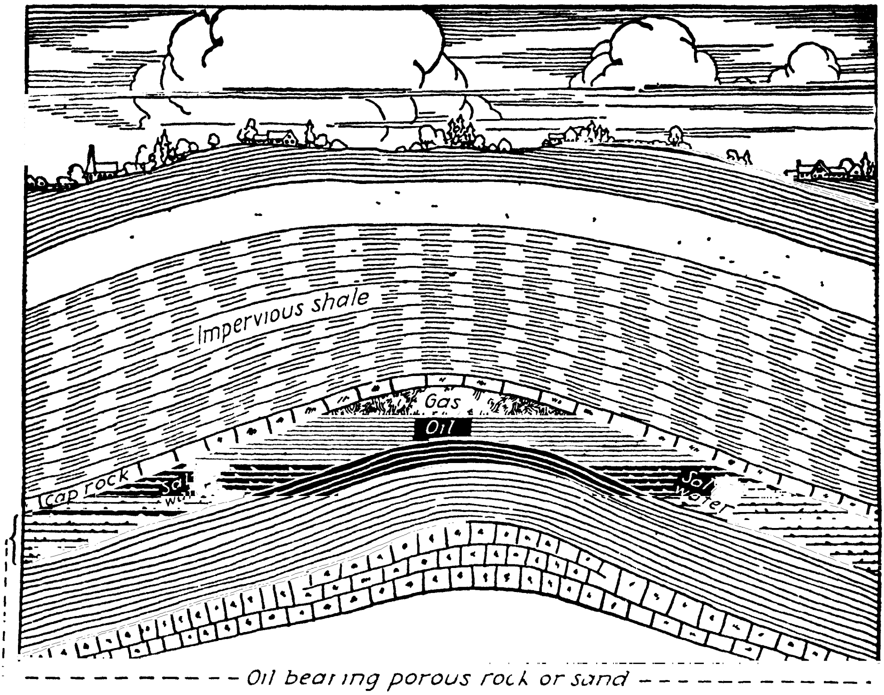

FIG. 1.—Oil trapped in nature's reservoir (*Courtesy of American Petroleum Institute*)

Production Statistics.—The world's production of petroleum from 1857 to January, 1941, aggregated over 37 billion barrels,[1] of which the fields in the United States produced approximately 60 per cent, as shown

[1] In the petroleum field a barrel holds 42 gal.

TABLE 1.—PRODUCTION OF PETROLEUM IN THE UNITED STATES,[a] 1857–1940

State	Thousands of Barrels
Texas	6,579,724
California	5,570,078
Oklahoma	4,805,911
Kansas	1,121,064
Louisiana	1,060,366
Pennsylvania	997,068
Illinois	698,813
Ohio	588,387
Arkansas	506,225
Wyoming	500,950
West Virginia	410,770
New Mexico	274,631
Kentucky	167,166
Michigan	145,117
Indiana	130,975
New York	118,777
Other states	129,029
Total	23,805,051

[a] "Petroleum Facts and Figures," 7th ed., p. 64, American Petroleum Institute, New York, 1941.

TABLE 2.—PRODUCTION OF PETROLEUM IN FOREIGN COUNTRIES,[b] 1857–1940

Country	Thousands of Barrels
Russia	4,394,952
Iraq	191,909
Iran	1,028,529
Venezuela	2,072,980
Rumania	917,558
Dutch East Indies	974,663
Mexico	1,986,801
Colombia	276,142
Peru	265,326
British India and Burma	302,324
Argentina	225,393
Trinidad	201,783
Poland	262,795
Sarawak and Brunei	101,175
Others	379,896
Total	13,582,326

[b] "Petroleum Facts and Figures," 7th ed., p. 16, American Petroleum Institute, New York, 1941.

in Tables 1 and 2. There is no industry that publishes more extensive statistical data than the petroleum industry,[1] through the American Petroleum Institute wherein the refiners, producers, and marketers have banded themselves together for presenting such data to the public. Table 3 gives a comparison of the total quantities of important refined products in the United States for the years 1937–1940.

Reserves and Raw Materials.—It may be questioned whether estimates of oil reserves are of any practical value, since they are admittedly of an extremely approximate nature. However, it should be apparent that some idea, although far from exact, of the available reserves of essential minerals—petroleum included—is of vital importance in mapping their development and the future trend of the related industries, particularly if a realization of these limitations is kept in mind. The following statements apply only to proved[2] oil reserves and leave out of consideration the questionable volume of the probable and possible oil reserves. It should be noted that only a fraction of the petroleum stored underground can be economically brought to the surface, that not all the oil brought to the surface is economically utilized, and that, although practically all the natural gas can be recovered and utilized, in actual practice a large part of the total volume of oil that reaches the mouth of a well is wantonly wasted. It has been estimated that, in the United States, only 25 per cent of the petroleum stored underground in proved fields is actually brought to the surface and that, in practice,

TABLE 3.—UNITED STATES PRODUCTION OF IMPORTANT REFINED PRODUCTS[a]
(Thousands of barrels)

Year	Gasoline	Kerosene	Gas oil and fuel oil	Lubricating oils	Wax[b]	Coke[b]	Asphalt[b]	Road oil
1937	519,051	65,308	458,770	35,321	1,863	6,533	23,001	8,087
1938	516,051	64,580	446,664	30,826	1,555	8,011	23,878	7,543
1939	556,895	68,521	467,690	35,036	1,659	8,332	27,248	7,868
1940	557,949	73,882	499,522	36,765	1,832	7,633	29,407	7,769

[a] "Petroleum Facts and Figures," 7th ed., p. 97, American Petroleum Institute, New York, 1941.

[b] 5.0 bbl. of coke are equal to one short ton, 7.14 bbl. of wax are equal to one short ton, 5.5 bbl. of asphalt are equal to one short ton

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[1] "Petroleum Facts and Figures," Department of Public Relations, American Petroleum Institute, New York, published yearly. This is a most unusual volume on statistics, presenting the industry from the point of view of utilization, production, refining, selling, and taxation. The facts are shown in tables and by pictorial representations. The U.S. Bureau of Mines also publishes generalized statistics on this industry.

[2] By proved reserves is meant the oil that is in known and proved fields and recoverable by present production methods.

approximately 25 per cent of the total gas produced is now wasted. Proved reserves of the world in January, 1936, were estimated at somewhat under 22 billion barrels. Table 4 lists the proved reserves in the United States in 1940; the proved world reserves in 1935 are given in Table 5. The proved reserves in the United States increased from 10 billion to 19 billion barrels between 1936 and 1941. Although the figures are not available, it is reasonable to assume that the foreign proved reserves have likewise increased, thus considerably increasing the world total.

TABLE 4.—PROVED OIL RESERVES IN THE UNITED STATES,[a] JAN. 1, 1941

State	Thousands of Barrels
Texas	10,623,516
California	3,291,382
Oklahoma	1,001,909
Pennsylvania, New York	252,648
Wyoming	304,821
Kansas	692,088
Louisiana	1,215,459
New Mexico	692,141
Illinois	315,305
Others	635,246
Total	19,024,515

[a] "Petroleum Facts and Figures," 7th ed., p. 74, American Petroleum Institute, New York, 1941.

TABLE 5.—PROVED OIL RESERVES IN FOREIGN COUNTRIES,[a] JAN. 1, 1936

Country	Thousands of Barrels
Russia	2,830,000
Iraq	2,475,000
Iran	2,150,000
Venezuela	1,350,000
Rumania	633,000
Dutch East Indies	450,000
Mexico	420,000
Colombia	275,000
Peru	138,000
British India	111,000
Argentina	92,000
Trinidad	91,000
Others	375,000
Total	11,387,000
United States	10,575,000
World total	21,962,000

[a] DUNSTAN, NASH, BROOKS and TIZARD, "Science of Petroleum," vol. 1, p. 533, Oxford University Press, New York, 1938.

In connection with the discussion of oil reserves, mention might be made of improved technique in the operation of oil wells. The concern of early operators with efficient methods of extraction and with the quantity of oil that ultimately would be left unrecovered in the reservoir sands, after the wells no longer could be operated profitably, was noticeably secondary. Ashburner, in 1887, estimated that wasteful producing operations in Pennsylvania and New York oil fields would leave ultimately eight to nine times as much of the original oil in the sands as would be recovered.[1] Laboratory experiments indicate that if early New York and Pennsylvania operators had been able to produce their oil in an economical manner, by methods now considered efficient, 2 to 2½ times more oil than was withdrawn from the sands might have been recovered by natural flow and pumping.[2]

The key to the problem is proper conservation and use of reservoir energy.[3] Oil is underlain by water under high head in the extraneous parts of the reservoir systems of most oil fields and overlain with gas, as diagrammatically shown by Fig. 1. The energy available to produce oil is represented by the head of water and the pressure of the gas acting on the oil. If the withdrawal of oil from the reservoir is at a sufficiently low rate, entrance of meteoric water at the outcrops and expansion of large water supplies already present tend to maintain the pressure head and supply the necessary energy.

An extremely important method of conservation is the return of natural gas to the oil wells. As an example, in the Sugarland, Tex., field, reintroduction of gas at a pressure of 1,400 lb. per sq. in. and a slower rate of production are expected to recover twice as much as would have been recovered under older methods of producing oil (a net recovery of 70 per cent of the original store).[4] Air mixed with the gas has certain disadvantages because it tends to deteriorate slightly the quality of the oil produced.

Water-flooding methods are responsible for the recovery of millions of barrels of oil that former production practices left in the reservoir sands. Water is usually introduced in a central well and allowed to extend gradually outward as an expanding circle to drive oil to surrounding wells. "Water flooding is estimated to have established a recoverable reserve of approximately 600,000,000 bbl. of oil in the

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[1] Ashburner, Petroleum and Natural Gas in New York, *Trans. Am. Inst. Min. Engrs.*, **16**, 915 (1887).

[2] Muskat, Wychoff, Botset, and Meres, Flow of Gas-liquid Mixtures through Sands, *Trans. Am. Inst. Mining Met. Engrs.*, **123**, 69 (1937).

[3] Miller and Shea, Gains in Oil and Gas Production Refining and Utilization Technology, p. 5*ff.*, *Tech. Paper* 3, National Resources Planning Board, 1941.

[4] Miller and Lindsly, Report on Petroleum Development and Production, Hearing on H.R. 441, 73d Cong., Recess, 1934, pt. II, p. 1207.

Bradford-Allegheny district that never could have been obtained by customary methods of production."[1]

For years oil wells drilled into hard limestone formations have been "shot" with nitro-glycerine because the resulting fissures and fractures increased the drainage of oil and gas into the well. Today, almost every well drilled into a limestone formation has the drainage channels enlarged by treatment with inhibited hydrochloric acid; sometimes in dense limestone the action of the nitro-glycerine is followed by acid treatment. This acid treatment has transformed many apparently nonproductive wells into rich producers. In the Illinois basin,[2] frequently wells drilled into oölitic limestone failed to show any oil until acid treatment was used. This acid treatment has become so important that it has now been given to about 10,000 wells in the carbonate rock (limestone and dolomite) regions of Michigan, Ohio, Illinois, Kentucky, Kansas, Oklahoma, Texas, and Louisiana. For this purpose about 25,000,000 gal.[3] of hydrochloric acid, containing an inhibitor to prevent corrosive action on iron, are consumed yearly.

The movement of oil in underground reservoirs is closely connected to the viscosity and surface tension of the oil. These in turn are related to the amount of gas dissolved in the oil. All this is a very practical application of Henry's law,[4] which states that at constant temperature, a liquid will dissolve the weight of a gas that is proportional to its pressure.

Transportation.—In the United States a great pipe-line transportation system moves a tremendous tonnage of petroleum. The pipe line has reached its maximum application east of the Rocky Mountains, where trunk lines, branch lines, and pumping stations form an extremely complex system. Also, in recent years there has been a large expansion in the mileage of pipe lines transporting natural gas. This expansion is closely related to the movement for conservation of petroleum and natural gas. It has been promoted also by the increased use of natural gas in cities distant from the source and as a factory chemical raw material. The pipe line is the only economical method yet discovered of transporting natural gas. At regular intervals pressure-booster stations are located, using a small part of the gas to drive gas engines connected to compressors.

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[1] MILLER and SHEA, *op. cit.;* STEIDLE, Some Basic Problems in the Conservation and Future Production of Pennsylvania Grade Crude Oil, *Oil Weekly*, p. 22, June 18, 1934.

[2] MILLER and SHEA, Report on Recent Progress in Petroleum Development and Production, p. 369, Petroleum Investigation (U.S. Congress, House of Representatives), Hearings on H.R. 290 and H.R. 7372 R, 76th Cong., 1939.

[3] KIESSLING, ROGERS, *et al.*, "Technology, Employment and Output per Man in Petroleum and Natural Gas Production," p. 150, Work Projects Administration, National Research Project in cooperation with U.S. Bureau of Mines, *Report* E-10, July, 1939.

[4] This matter is well treated with references to the original literature on pp. 17–25 of Miller and Shea, Gains in Oil and Gas Production, etc.

Tank ships are the "water pipe lines" that connect remote oil fields with the refineries and markets. As an efficient and cheap means of bulk transportation, particularly over long distances, they are cheaper than the pipe line on land. The refined products of the industry are transported by an occasional special pipe line and by thousands of tank cars and motor tank trucks. Huge steel or concrete reservoirs holding 100,000 bbl. or more are employed for the storage of petroleum and its products. Despite a tremendous potential fire hazard, the loss through fire is among the smallest of industrial fire losses, owing to care, forethought, and many automatic protective devices.

Earnings and Investment.—Contrary to the popular conception of petroleum as "liquid gold," the total income of the industry has been moderate. Such profits as have accrued have been more the reward of business enterprise and sound research than of good fortune. In the 17 years from 1923 to 1939, a period covering both booms and depressions, the annual rate of return on net worth averaged 5.91 per cent,[1] in comparison with 7.61 per cent from the manufacturing industries. The large investment in the petroleum field is summarized in Table 6. The subdivisions of this tabulation, in a very enlightening manner, show the varied nature of this extensive business.

TABLE 6.—NET INVESTMENT IN UNITED STATES PETROLEUM INDUSTRY, 1937[a]

Division	Net plant investment	Per cent of total	Investment including other assets[b]	Per cent of total
Crude-oil production	$3,210,000,000	51.4	$3,740,000,000	47.4
Crude-oil pipe lines	458,400,000	7.3	506,500,000	6.4
Marine transportation	206,000,000	3.3	226,600,000	2.9
Refining	848,500,000	13.6	1,400,000,000	17.7
Tank cars	105,000,000	1.7	112,500,000	1.4
Refined-products pipe lines	48,850,000	0.8	54,000,000	0.7
Marketing	1,267,000,000	20.3	1,752,000,000	22.2
Segregated administration	100,000,000	1.6	100,000,000	1.3
Total	$6,243,750,000	100.0	$7,891,600,000[c]	100.0

[a] "Petroleum Facts and Figures," 7th ed., p. 178, American Petroleum Institute, New York, 1941.

[b] Principally inventories of crude oil and products, and net working capital.

[c] No complete later data available, but it was estimated that the total net investment increased to about $8,200,000,000 in 1939.

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[1] "Petroleum Facts and Figures," p. 178.

CONSTITUENTS OF PETROLEUM, INCLUDING PETROLEUM GASES

Crude petroleum is made up of hundreds of different individual chemicals from methane to asphalt. Although most of the constituents are hydrocarbons (83 to 86 per cent of carbon), the ultimate analyses indicate the presence in small quantities of nitrogen (0 to 2.5 per cent), sulfur (0 to 4 per cent), and oxygen (0 to 3.5 per cent).[1] The refining of petroleum separates the constituents into various cuts or fractions distinguished by properties useful in the sale of the fraction, such as boiling range and viscosity.

The hydrocarbons[2] may be divided into two chemical classes:

1. OPEN CHAIN OR ALIPHATIC COMPOUNDS, comprising:

Paraffin Series, C_nH_{2n+2}.—This series of hydrocarbons comprises a larger fraction of most petroleums than any of the other individual classes.

Olefin Series, C_nH_{2n}.—This series is not present or only in very small quantities. Cracking processes produce large amounts of olefins. Olefins are very useful because of their excellent antiknock properties and chemical reactivity.

Diolefin Series, C_nH_{2n-2}.—The quantity of diolefins found in crude petroleum is exceedingly small. Many crudes do not contain sufficient amounts for identification.

2. RING COMPOUNDS, comprising:

Naphthene or Cycloparaffin Series, C_nH_{2n}.—This series, which has the same type formula as the olefin series, differs in that its members are completely saturated. Cyclohexane, C_6H_{12}, is a member of this series. It is the second most abundantly occurring series of compounds in most crudes.

Aromatic or Benzene, C_nH_{2n-6}.—Although only traces of aromatic compounds are present in most petroleums, the Borneo and Sumatra crudes contain relatively large amounts. These compounds are produced by chemical reactions and, like the olefins, have high antiknock qualities.

The three general classes[3] of petroleum crudes are as follows:

1. *Paraffin Base*.—These crudes consist primarily of open-chain compounds.

2. *Naphthene Base*.—These crudes contain a high percentage of cyclic (naphthenic) compounds.

3. *Mixed Base*.—These crudes contain large quantities of both paraffinic and naphthenic compounds.

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[1] See NELSON, "Petroleum Refinery Engineering," 2d ed., p. 29, McGraw-Hill Company, Inc., New York, 1941, for chart and further details.

[2] FAUST, Hydrocarbon Chemistry for The Refinery Worker, *Petroleum Refiner*, **21**, 229 (1942); TRUSTY, Hydrocarbon Structure of Petroleum Is Complex, *Petroleum Refiner*, **21**, 257 (1942).

[3] Another classification in use depends for its basis upon the type of residue left after primary distillation of the petroleum. *Paraffin base* denotes a paraffinic lubricating oil residue and *asphalt base* an asphaltic residue.

Petroleum has long been divided into salable cuts by *fractionation* in the refining operations. This is a separation by boiling ranges. Indeed, the natural separation that takes place when the petroleum leaves its underground reservoirs, into natural gas and ordinary crude, is based on the same principle. Such refinery fractions may be classified roughly as follows:

- Natural (or casing-head) gasoline and natural gas.
- Light distillates.
  - Motor gasolines.
  - Solvent naphthas.
  - Kerosene.
  - Light furnace oils.
- Intermediate distillates.
  - Heavy furnace oils.
  - Diesel oils.
  - Gas oils.
- Heavy distillates.
  - Heavy mineral oils (medicinal).
  - Heavy flotation oils.
  - Waxes (candles, sealing, insulating).
  - Lubricating oils (large range).
- Residues.
  - Lubricating oils.
  - Fuel oils.
  - Petrolatum.
  - Grease.
  - Road oils.
  - Asphalts.
  - Coke.

Natural gas occurs as accumulations in underground, porous reservoirs either with or without petroleum oil. Though natural gas has been known for centuries, not until the early 1800's was it first discovered in the United States; since that time it has become one of this country's great industries. Many of our finest gas fields were wasted in the process of securing crude oil, before it became apparent that the natural gas itself was a valuable product. Progress is being made in the conservation of natural gas, however, and legislation has been enacted prohibiting the stripping of "wet" gas for its small gasoline content and then wasting the gas. The total production of natural gas in the United States in 1943 was about 3,250 billion cubic feet, compared to 1,935 billion in 1935 and 1,555 billion in 1933. The present annual consumption of natural gas in the United States is valued at more than $500,000,000. In spite of the great waste of natural gas[1] and the fact that at our present rate of consumption our potential reserve should last only about 30 or 40 years more, new discoveries, improvements in utilization, and reduction in waste will extend our supply for a much longer time. Natural gas is composed chiefly of hydrocarbons of the paraffin series from methane up to pentane, carbon dioxide, nitrogen, sometimes helium, but few if any unsaturated hydrocarbons. The most important products obtained from natural gas are fuel, natural gasoline, liquid gas, carbon black, helium, hydrogen, and carbon monoxide. However "wet" natural gas is a most important present and *potential* raw material for many other chemicals such as acetic acid, ethylene, acetone, formaldehyde, methanol, and higher alcohols (see Chap. VII, especially Table 1).

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[1] LEVEN, "Done in Oil," p. 588, Ranger Press, New York, 1941; PEW and DOTTERWEICH, Maximum Hydrocarbon Utilization with Natural Gas as a Chemical Raw Material, *Petroleum Refiner*, **23**, No. 4, 96 (1944).

Natural Gasoline.—Gasoline extracted from natural gas is differentiated from straight-run or refinery gasoline (which is distilled from crude oil) by the term *natural* or *casing-head* gasoline. The recovery of natural gasoline from natural gas has given us a highly volatile gasoline for blending into a motor fuel, particularly for easy starting in cold weather. Gasoline in natural-gas pipe lines was first discovered in the early 1880's, and steps were taken to recover it. However, there was no market for it at the time, and the methods of recovery were crude, consisting merely of cooling the gas under normal pressure. Today there are about 680 plants valued at $325,000,000 which produce about 12,000,000 gal. per day of natural gasoline.[1]

When crude oil is forced from a well by the pressure of the natural gas, some of its lighter components are vaporized into the gas. Consequently, the composition and characteristics of the recovered natural gasoline are determined by the composition of the oil. The first commercial process for the recovery of natural gasoline was by means of *compression cooling.* Later, the natural gas was passed through adsorption towers containing *activated carbon*, but today the natural gasoline is *absorbed* by a low-boiling *gas oil* which is then heated and stripped of the gasoline by steam. Some of the recent plants combine compression and absorption. The recovered gasoline is "stabilized" or fractionated under pressure to remove the light, high-vapor-pressure components which comprise usually 10 to 30 per cent of the raw gasoline, as shown in Fig. 2.[2] The primary use of natural gasoline is for blending with refinery products to make motor fuel. Natural gasoline plants are now producing large quantities of pure isobutane and isopentane for alkylation with light olefins as ethylene, propylene, or butylene to furnish aviation gasoline. Similarly, from natural gasoline stabilizers, propane and butane are available. The propane is cracked to propylene (propene) and alkylated to high-octane gasoline; or esterified to isopropyl acid sulfate and hydrolyzed to isopropyl alcohol which is dehydrogenated to acetone. The butane serves by dehydrogenation to furnish butadiene for synthetic rubber or butene for alkylation.

Cracked or Refinery Gases.—Natural gas is particularly devoid of unsaturated hydrocarbons, hydrogen, and carbon monoxide; these compounds are, however, present in the cracked gases of refineries.[3] Because of the large quantities of unsaturated and hence chemically reactive hydrocarbons produced by cracking processes, the oil industry is now developing along the line of synthesis. The olefin hydrocarbons of these cracked gases are used in the manufacture of polymerized and alkylated gasoline, antifreezes, explosives, solvents, medicinals, fumigants, resins, synthetic rubber, and many other products. When olefins are not available in sufficient amounts, they are made by dehydrogenation of paraffins.

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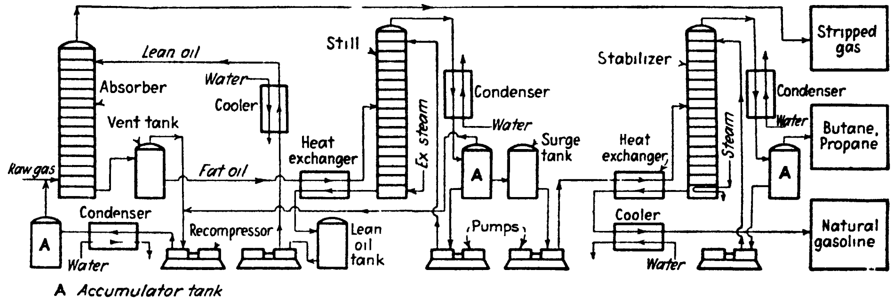
[1] LEVEN, *op. cit.*, p. 597.

[2] NELSON, *op. cit.*, p. 545.

[3] Analyses are given in Perry, *op. cit.*, p. 2366.

Liquefied Petroleum Gases.—Light hydrocarbons such as propane and butane, which are produced as a by-product from rectifiers treating natural gasoline to meet lower-vapor-pressure requirements, are now finding wide use as "bottled" or liquefied gas. Some of the gas is removed in the liquid form and only need be placed in pressure cylinders for transportation; the remainder is used in the refinery as raw material for chemical synthesis with any leftovers (decreasing) serving for fuel. The water content of the fuel should, however, be limited because such water may become frozen and clog the vaporizing apparatus of the cylinder. The water allowed is 10 parts water vapor per 1,000,000 parts. From 1933 to 1942, the production of liquid petroleum gas increased from 39,000,000 to 555,000,000 gal. per year.[1] Of the 1942 consumption, 265,000,000 gal. were consumed domestically, 262,000,000 gal. industrially, and 27,000,000 gal. for city gas. Since the heating value of the pure gas is so high, it is often mixed with an inert gas before using. Liquefied petroleum gases are competitive with many types of fuel in present use. Bottled gas is used by many rural dwellers, who are too



Natural gas (150 lb pressure)	20 000 000 cu ft	Per 24 hr day, producing 10000 gal gasoline
Absorption oil recirculation per day	150,000 gal*	
Steam	60 000 lb	
Water	200,000 gal	
Electricity	20 kw hr	
Direct labor	42 man hr	

**Loss approx 6 gal per 1,000 gal gasoline produced (Dykema & Chenoweth, Bur Mines Tech Paper No. 263)*

FIG. 2.—Natural gasoline obtained by absorption and compression. (*Courtesy of Burrell-Mase Engineering Company*)

far from any gas mains, for cooking, lighting, heating water, and gas refrigeration. Its cost for domestic use is high, ranging from 4 to 14 cents per pound, but its convenience and service warrant this price, which is caused largely by container and delivery expenses.

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[1] NELSON, *op. cit.*, p. 544; OBERFELL, Liquified Petroleum Gas in 1942, *Petroleum Refiner*, **22**, 100 (1943); ROHMAN and KRAPPE, "Handbook Butane-Propane Gases" Western Business Papers, Inc., Los Angeles, 1943, bibliography.

PRODUCTS OF REFINING

Light Distillates.—These embrace naphthas and refined oils, aviation gasoline, motor gasoline, petroleum solvents, and kerosene. Gasoline is the most important of these; it is the most important petroleum product. With the advent of high-compression motors, the tendency of a fuel to knock, or detonate violently (thought to be due to autoignition of part of the compressed charge in front of the flame), has become increasingly important. Certain substances such as lead tetraethyl[1] and iron carbonyl[2] tend to prevent knocking. *Octane number* is the percentage of isooctane (2,2,4-trimethylpentane) in a mixture with normal heptane, which as a sample fuel will give the same knocking characteristics as the gasoline in question. Aviation gasoline with an octane number of 100 or even higher, is largely the result of blending together aliphatic and aromatic compounds with lead tetraethyl. The amount of sulfur that can be safely allowed in gasoline is a controversial question. Quantities as high as 0.2 per cent will not cause serious corrosion; the quantity of sulfur is usually limited by state regulation to 0.1 per cent. Sulfur in low percentage markedly reduces the effect of tetraethyl lead in increasing the octane number. The color of a gasoline indicates little about its quality. Most refiners resort to the use of oil-soluble dyes to mask the off-white color of the cracked product.[3] The dye also serves to identify a gasoline and promote confidence in its advertised qualities. The demand for ordinary and aviation gasoline[4] has stimulated the natural gas industry and the cracking and polymerization processes which will be discussed later. The term *naphtha* refers to any light oil product having properties intermediate between gasoline and kerosene. Naphthas are extensively used as commercial solvents in paints and for dry cleaning. Kerosene is commonly consumed as a fuel and in some cases for illuminating purposes. Light furnace oils are employed as fuel in home heating plants.

[1] MIDGLEY, Tetraethyl Lead, *Ind. Eng. Chem.*, **17**, 827 (1925).

[2] Used in Germany.

[3] EGLOFF, *et al.*, Dyes to Reduce Loss in Acid Treatment, *Oil Gas J.*, **29**, No. 42, 133 (1931).

[4] ANON., High-octane Aviation Gasoline Program Continues to Expand, *Chem. & Met. Eng.*, **50**, No. 6, 129 (1943), excellent flow chart showing relationships of "unit processes" *e.g.*, alkylation, isomerization, and polymerization; VAN WINKLE, Production of Hydrocarbons for Aviation Motor Fuels, *Petroleum Refiner*, **22**, 273 (1943), specifications, compositions, reactions, processes, references, and excellent summary.

Intermediate Distillates.—These include gas oil, heavy furnace oil (domestic), cracking stock, Diesel fuel oil, and absorber oil. Distillates are cheap. Hence in the refinery any excess stocks are disposed of by cracking or reforming into cracked gasoline. Distillates are difficult to crack but produce excellent cracked products. Often they are blended with heavy tar to reduce the viscosity of the tar so that it can be marketed as a fuel oil. Certain special heavy naphthas are used to reduce the viscosity of asphalt so that it can be readily applied as road oil; such material is known as *cutback asphalt.* Originally, gas oil was widely used for enriching artificial gas, but today most of it is used as a fuel or cracked into gasoline. Diesel fuel is a special grade of gas oil which has become a most important specialty in recent years. The proper viscosity of Diesel fuel is very essential and should be held within rigid limits. Distillates may also be used as vehicles for insecticides.[1]

Heavy distillates comprise lubricating oils (also from residues), heavy oils for various purposes, and waxes. The field of lubricating oils is too broad to permit a complete discussion of it here. The S.A.E.[2] has greatly assisted in classifying oils by introducing a number system based on viscosity and change in viscosity with temperature (viscosity index). Such tests as flash point, viscosity, pour point, emulsibility, and carbon residue are useful in determining the application to which an oil may be put. Table 7 gives interesting data regarding the kind of crude oil used in manufacturing lubricating oils.

Paraffin wax is classified according to the melting point. Refined wax is white wax made free from odor or taste by agitation with sulfuric acid.

TABLE 7.—CRUDE OIL USED IN MANUFACTURING LUBRICATING OILS[a]

Type of crude	Per cent of production	Average percentage recovery from crude	Percentage of crude processed for lubricants
Mixed base	32	20	9.1
Paraffin base	30	30	100
Coastal crude	31	30	32.4
California crude	7	20	5.

[a] NELSON, "Petroleum Refinery Engineering," 2d ed., p. 150, McGraw-Hill Book Company, Inc., New York, 1941.

Residues include asphalt, fuel-oil residual, greases, coke, petrolatum. These are merely by-products or residues from the regular refining processes. Petroleum coke is used commercially for electrodes, in the manufacture of calcium carbide, in paints, and in the ceramics industry. Asphalt, also of great importance, finds employment as a road or roofing material or for waterproofing structures. The properties of asphalt may be markedly altered by heating it to a high temperature and partly oxidizing it by blowing air through it. Such material is more viscous and less resilient than ordinary asphalt, is known as *blown* asphalt, and is widely used in the manufacture of roofing and for grouting. Very hard asphalt finds some use as a briquetting binder.

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[1] NELSON, *op. cit.*, p. 145.

[2] Society of Automotive Engineers.

Greases constitute a large group of different materials and may be grouped into three classes[1]:

1. Mixtures of mineral oil and solid lubricant.
2. Blends of waxes, fats, resin oils, and pitches.
3. Soap-thickened mineral oils.

Specialties.[2]—More and more attention is being paid to the field of petroleum chemistry. Among the many possible petroleum derivatives may be mentioned explosives, soaps, antiseptics, chlorinated products, lacquers, varnishes, organic acids, refrigerants, and rubber substitutes.[3] Toluene is now being synthesized in larger quantities from petroleum than from coal tar.[4]

REFINING OR MANUFACTURE

The general characteristic of petroleum refining has been a most unusually economical processing of crudes to consumer products. It seems hardly possible that the average price received by refiners for gasoline is around 5 cents per gallon. The difference between what the consumer pays and the refiner receives is caused by taxation and the cost of retailing.

The initial refining embraced primary distillation, which involves the unit operations of fluid flow, heat transfer, and distillation. Indeed, the necessity of studying these manufacturing aspects in the petroleum field was a great stimulation to the development of this phase of chemical engineering. These purely physical transformations were early supplemented by chemical reactions in the further *refining* of petroleum products. But the great stimulation to the employment of chemical change in the manufacture of petroleum products came with the growing consumption of gasoline in excess of that supplied by straight distillation. This situation, developing after 1912, forced the application of pyrolysis to petroleum products wherein, by what the industry calls *cracking*, the long molecules were broken down into smaller ones suitable for gasoline. Although cracking, with or without catalysts, is still the most important chemical change taking place in the petroleum industry, yet in recent years, to meet the demands for better gasoline, or for alcohol, acetone, or rubber chemicals from petroleum, other chemical changes have been applied on a large scale. Among these we may list alkylation, isomerization, polymerization, hydrogenation, cyclization, dehydrogenation, and esterification (see Unit Processes, page 818).

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[1] SIMPSON and WILCH, The Manufacture of Grease, *Refiner Natural Gasoline Mfr.*, **10**, No. 3, 77 (1931).

[2] See unit processes, p. 818.

[3] NELSON, *op. cit.*, p. 156; STRATFORD, The Advancing Front of Petroleum Chemicals, *Chem. Industries*, **53**, 489 (1943).

[4] See the unit process of aromatization (hydroforming), p. 831.

It is a long step from the initial shell-still topping[1] gasoline and other like products from the crude, to the modern continuous complicated refinery wherein 20,000 bbl. or more per day of crude, day in and day out, enter the processing equipment by way of the pipe stills and are separated in the continuous bubble-cap towers into the various constituents from gas through gasoline, kerosene, gas oil, lubricating oil, down to fuel oil, residuums, or tars. Such refineries are also equipped to carry on many of the secondary treatments in a continuous manner. Naturally each individual treatment depends on the type of base, an asphalt base requiring different treatment from a paraffin base. Furthermore, designs vary with market demand. With modern increased demand for gasoline, manufacturing procedures naturally are adapted to obtain a maximum yield of gasoline.

Energy Changes.—The energy changes involved in petroleum refining are both mechanical and chemical. Some of the unit processes are exothermic reactions though most are endothermic. In addition to the heat[2] that must be supplied for cracking, distillation, and the other processes, large amounts of mechanical energy are needed for pumping, compressing gases, and the like.

Unit Operations.—In theory, the processes of oil refining are fairly simple; in actual practice they are quite complicated. The typical refinery consists of one or more units called *stills* which include a furnace, an oil heater of the tube type, a bubble tower, steam strippers, heat-exchange equipment, coolers, and condensers; working storage tanks at the unit; batch agitators or continuous closed-tank units for treating the products to remove deleterious compounds of sulfur and give acceptable color; filters; blending and mixing tanks for loading; a piping system for the receipt of crude oil; pumps for the transfer of oils and for loading and shipping products; storage tanks for crude oil supply and finished product; a vapor recovery system and many auxiliaries. A power plant for generation of steam and perhaps electric power and light should also be included.

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[1] Topping involves the simple distillation of the more highly volatile materials, or what may be called *tops*, from the crude oil.

[2] The following references bear on this subject: NELSON, *op. cit.*, pp. 297*ff.*, for heats of cracking; pp. 192–200, for typical calculations of heat balances; GRUSE and STEVENS, "The Chemical Technology of Petroleum," 2d ed., pp. 432*ff.*, for thermodynamic data for petroleum hydrocarbons; pp. 210*ff.*, for latent heats of evaporation and specific heats, McGraw-Hill Book Company, Inc., New York, 1942; PERRY, *op. cit.*, pp. 1345–1352, for distillation data and specific heats; "Science of Petroleum," vol. 2, p. 1256.

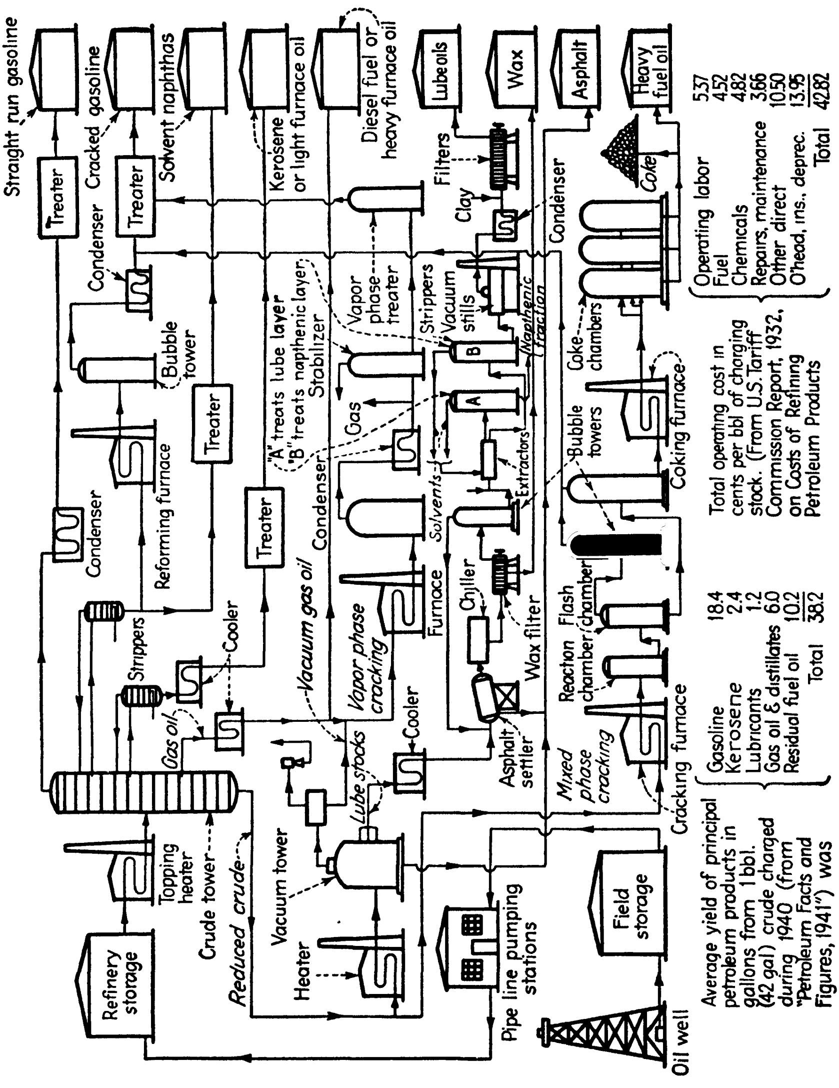

FIG. 3.—Generalized over-all flow sheet from oil well to salable products.

In the operation of this large entity, heat, energy, and material balances are of utmost importance in keeping a rigid control upon all steps in the processing of the oil.

A presentation of the more important unit operations follows:

Fluid Flow.[1]—The petroleum engineer has turned to the comprehensive literature on fluid flow of water and suitably revised this information for petroleum. Two important differences between oil and water should be recognized: oils exhibit wide change of viscosity with temperature and wide range of viscosity, and they are sensitive to heat.

Heat Transfer.[2]—The solution of this problem is somewhat complicated because of lack of complete data. In general, the use of empirical results will be desirable. Equipment should be cleaned regularly to maintain satisfactory heat transfer. The large quantities of cooling water used generally make cooling towers and water-treating equipment essential.

Distillation.[3]—This ranks with heat transfer as being among the more important of unit operations. The older operations of batch distillation have now been almost entirely superseded by continuous ones. The present system involves heating the crude by pumping it through tubes placed inside a furnace (tube still) and then allowing it to vaporize in a fractionating column, which is tapped at several points allowing continuous side draw of the various boiling "fractions" or products. The residuum withdrawn from the bottom of the column may be subjected to a vacuum or steam distillation. Figure 3 is a schematic drawing of a modern refining group showing the separation of the crude into the various fractions and the subsequent treatment of each fraction. Several products are removed from the crude tower as shown. The kerosene and naphtha fractions contain small amounts of imperfectly separated straight-run gasoline of higher volatility than the main fraction. These are removed in strippers (short columns containing only a few plates) by blowing in steam. The gasoline vaporizes out the top of the stripper and is returned to the crude tower.

Absorption.[4]—Absorption is generally used to separate a higher boiling constituent from other components of a system of vapors and gases. Usually the absorption medium is a special gas-oil cut. Absorption is widely employed for the recovery of natural gasoline from well gas and for the recovery of vapors given off from storage tanks. The absorbed products are recovered by fractionating or steam stripping.

Adsorption.[5]—Adsorption is employed for about the same purpose as absorption; in the process just mentioned natural gasoline may be separated from the natural gas by adsorption on charcoal. Adsorption is also used to remove undesirable colors from lubricating oil, usually with activated clay.

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[1] PERRY, *op. cit.*, pp. 788–946.

[2] PERRY, *op. cit.*, pp. 947–1029.

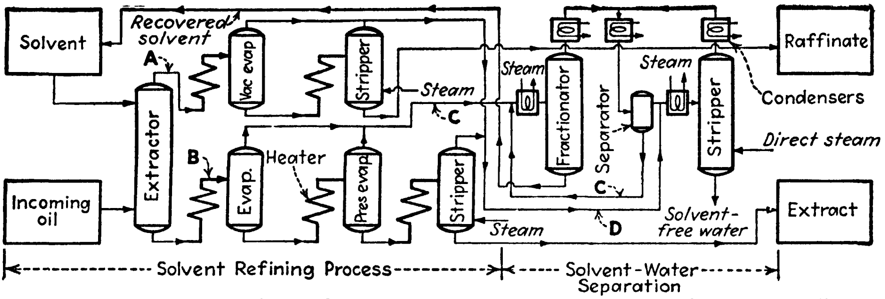
[3] PERRY, *op. cit.*, has an entire section on distillation, pp. 1337–1478. This should be consulted for many references to literature, presentation of fundamental principles, and applications.

[4] PERRY, *op. cit.*, pp. 119–1212.

[5] PERRY, *op. cit.*, pp. 1269–1336; especially pp. 1278–1291 (clays), 1318 (natural gasoline).

Filtration.[1]—Filtration after chilling is the usual method for removal of wax from wax distillate. The mixture of wax and adhering oil obtained from the press is frozen and allowed to warm slowly so the oil drains (sweats) from the cake, thus further purifying the wax. "Contact" filtration, involving the use of clay, is the common method of purification of oils; decolorization takes place at the same time. (This is an adsorption phenomenon.)

Extraction.—This involves the removal of a component from a liquid by means of the solvent action of another liquid. The procedure of extraction by means of solvents is becoming increasingly important in the further refining of lubricating oils. A recent development is the production of toluene by extraction from a specially processed petroleum. Low viscosity-index hydrocarbons and some colored materials may be removed in this way from lubricating oil. Usually the extraction is countercurrent. Two problems are involved: obtainment of solution equilibriums and separation of the two immiscible phases.



Key: A = Raffinate and solvent; B = Solvent extract and water; C = Solvent saturated with water D = Water saturated with solvent

FIG. 4.—Typical solvent-refining process employing furfural and provided with solvent-water separation and recovery.

Figure 4 shows a typical solvent refining[2] process for lubricating oil. The oil is mixed with the solvent or solvents in an extractor. If a proper solvent has been chosen, the mixture separates into two layers: one rich in solvent and containing the dissolved impurities (extract); the other containing little solvent and most of the desirable high-viscosity oil (raffinate).

The procedure as shown in Fig. 4 involves the following *unit operations* when furfural is the solvent:

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[1] PERRY, *op. cit.*, pp. 1653–1698, especially p. 1689.

[2] ANON., Furfural Refining of Lubricants, *Chem. & Met. Eng.*, **47**, 859 (1940), pictured flow sheet; "Rogers' Manual of Industrial Chemistry," 6th ed., pp. 565–574; D. Van Nostrand Company, Inc., New York, 1942; PERRY, *op. cit.*, p. 1231.

Continuous countercurrent extraction of the lubricating stock with furfural at temperatures between 130 and 280°F., depending on the oil used; provided with suitable heat exchangers.

Continuous separation of raffinate fraction from extract fraction.

Recovery of solvent (furfural) by vacuum evaporation from raffinate or refined oil.

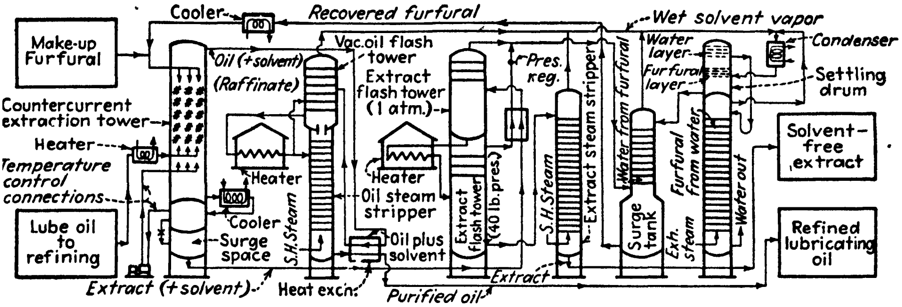

FIG. 5.—Flow sheet for lube oil refining by furfural extraction.

Stripping by steam distillation of small amounts of remaining solvent from refined oil, giving wet furfural or water solution of furfural.

Recovery of solvent (furfural) from extract by atmospheric and by pressure distillations, this wet solvent (furfural) being the main recovery; fractionation leaves dry solvent behind and ready for reuse.

Stripping by steam of small amounts of solvent left in extract, furnishing wet solvent or water solution of solvent.

Final stripping of solvent from combined aqueous solutions. The overhead is chilled, and the solvent is conducted to fractionator.

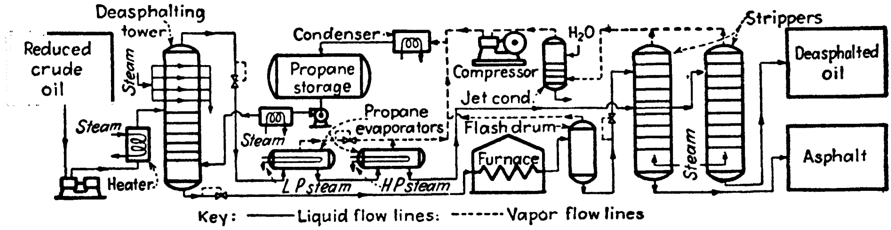

FIG. 6.—Flow sheet for lube oil deasphalting—Kellogg tower process.

When furfural is used, the solvent is recirculated through the system as many as fifteen times each day and with the very small solvent loss of less than 0.05 per cent of total solvent turnover (see also Fig. 5).

Other solvents frequently used are liquid sulfur dioxide, propane and cresylic acid, dichloro-ethyl ether, phenol, and nitro-benzene.[1] Solvents are also widely employed for removing the wax from lubricants and thus lowering the pour point.[1] Figures 6 and 7 present typical lubricating oil purifications.

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[1] NELSON, *op. cit.*, pp. 616–625.

Unit Processes.—Petroleum offers such a fertile field for chemical synthesis that it is difficult to list all the unit processes that may be applied to this raw material. The following examples are a few of the more important basic reactions:[2]

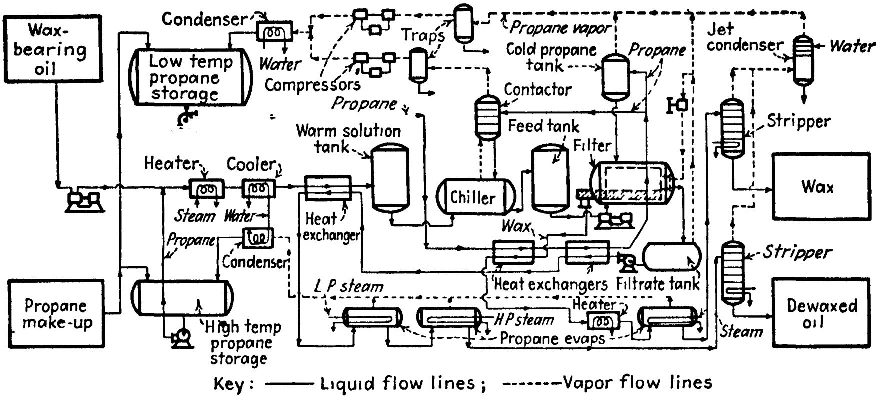
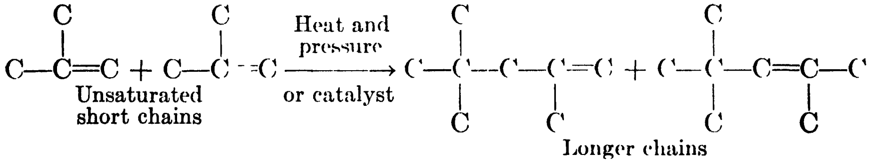


FIG. 7.—Lube oil dewaxing—Kellogg propane process.

1. *Cracking or Pyrolysis* (see Figs. 8 to 13):

$$\underset{\substack{\text{Long-chain}\\ \text{hydrocarbons}}}{\text{C—C—C—C—C—C—C}} \xrightarrow[\text{or catalyst}]{\substack{\text{Heat and}\\ \text{pressure}}} \underset{\substack{\text{Short-chain}\\ \text{hydrocarbons}}}{\text{C—C—C} + \text{C=C—C—C}}$$

2. *Polymerization* (see Fig. 14):



$$\underset{\substack{\text{Unsaturated}\\ \text{short chains}}}{\text{C—}\overset{\text{C}}{\overset{|}{\text{C}}}\text{=C} + \text{C—}\overset{\text{C}}{\overset{|}{\text{C}}}\text{=C}} \xrightarrow[\text{or catalyst}]{\substack{\text{Heat and}\\ \text{pressure}}} \underset{\text{Longer chains}}{\text{C—}\underset{\underset{\text{C}}{|}}{\overset{\overset{\text{C}}{|}}{\text{C}}}\text{—C—}\underset{\underset{\text{C}}{|}}{\text{C}}\text{=C} + \text{C—}\underset{\underset{\text{C}}{|}}{\overset{\overset{\text{C}}{|}}{\text{C}}}\text{—C=}\underset{\underset{\text{C}}{|}}{\text{C}}\text{—C}}$$

3. *Alkylation*[3] (see Fig. 16):

$$\text{Unsaturated} + \text{isosaturated} \xrightarrow{\text{catalyst}} \text{saturated branched chain,}$$ *for example:*

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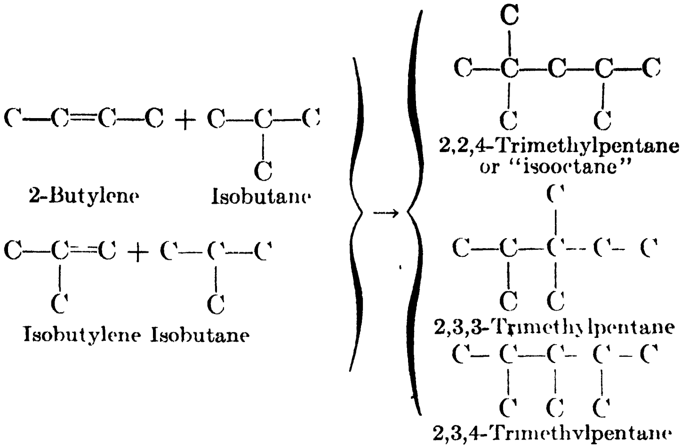
[1] ANON., Solvent Dewaxing of Lubricants, *Chem. & Met. Eng.*, **48**, No. 10, 106 (1941), pictured flow sheet employing methylethylketone and benzene.

[2] GRUSE AND STEVENS, *op. cit.*, Chap. 3, "Group Reactions in Petroleum Oils" and "Derived By-products," p. 646.

[3] MURPHREE, War Developments in the Petroleum Industry, *Ind. Eng. Chem.*, **35**, 626 (1943).

Catalytic alkylation.—


2-Butylene Isobutane

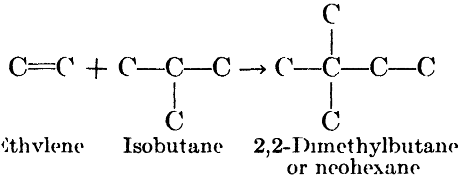
Isobutylene Isobutane

2,2,4-Trimethylpentane or "isooctane"

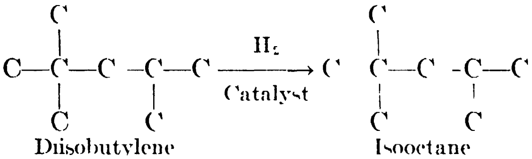
2,3,3-Trimethylpentane

2,3,4-Trimethylpentane

Thermal alkylation.—


Ethylene Isobutane 2,2-Dimethylbutane or neohexane

4. *Hydrogenation:*



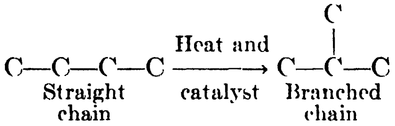
Diisobutylene Isooctane

5. *Chlorination:*

$$C_5H_{12} + Cl_2 \rightarrow C_5H_{11}Cl + HCl$$

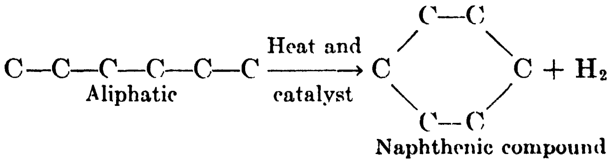
Pentanes Chloro-pentanes

6. *Isomerization:*



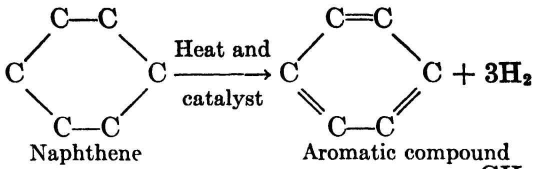
Straight chain Branched chain

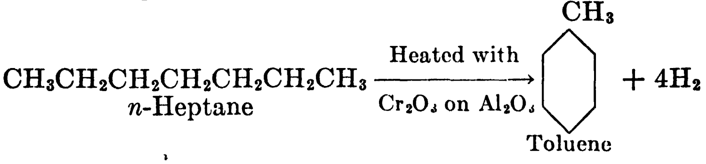
7. *Cyclization:*



Aliphatic Naphthenic compound

8 *Hydroforming or Aromatization:*





Cracking or Pyrolysis.—Cracking[1] (pyrolysis) is the process of converting large molecules into smaller ones by the application of heat and/or catalysts. A significant amount of polymerization of these smaller molecules also occurs.[2]

$$CH_3(CH_2)_{12}CH_3 \rightarrow CH_3(CH_2)_5CH_3 + CH_3(CH_2)_4CH{=\!=}CH_2$$

This equation is a highly simplified example of this process, for the original molecule may be broken at any one of the carbon-carbon bonds and usually with carbon formation. Thus, in cracking one pure compound, such as tetradecane, several products (heptane, heptene, hexane, octane, butane, butenes, carbon, etc.) are formed. In cracking the mixture of compounds occurring in petroleum the number of possible products is so great that the representation of the process by simple equations is impossible.

The heat of decomposition of petroleum is difficult, if not impossible, to calculate accurately, owing to the lack of necessary data. In the cracking reaction, if large amounts of gas are produced, the heat of decomposition is endothermic and relatively high. Also, the heat of reaction is often lower than theoretical owing to the exothermic reforming of some of the cracked products.[3]

"The cracking process," according to Egloff,[4] "is the greatest force for conservation that has been developed in the oil industry." Cracking is of two kinds: thermal and catalytic. In the early days of *thermal cracking*, gas oil was used as the charging stock. More recent technological developments have advanced the technique of cracking, making possible its adaptation to a wide range of materials from naphthas to heavy crude residuums. In the combination distillation-cracking unit, crude oil from the storage tanks is separated into various fractions directly, and the resulting fractions are cracked in continuous operations. Selective cracking operations with a high degree of flexibility have been made possible by multiple heating coils, operated under temperatures ranging from 900 to 1100°F. and pressures from 600 to over 1,000 lb. per sq. in. Charging stock is cracked to produce high antiknock gasoline, tractor fuel, furnace oil, heavy fuel oil, metallurgical coke, and large volumes of by-product gases. Today, total gasoline yields of 70 to 85 per cent[1] are obtained from the crude oil and approximately one-half of the country's gasoline is produced by cracking. In 1938, 270,471,000 bbl. of cracked gasoline were manufactured.[2] See Fig. 3 for generalized relationships of cracking in the petroleum industry.

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[1] GRUSE and STEVENS, *op. cit.*, Chap. 10, p. 354.

[2] NELSON, *op. cit.*, p. 289.

[3] NELSON, *op. cit.*, p. 297, discusses this subject and gives examples of typical calculations.

[4] EGLOFF, 300 Years of Oil, *Ind. Eng. Chem.*, **27**, 648 (1935); "Rogers' Manual of Industrial Chemistry," p. 533.

A most significant recent advance is *catalytic cracking*, which produced 700,000 bbl. of aviation fuel in 1937 and 1938[3] and has tremendously expanded since then to meet the demands of the Second World War. Cracking by the thermal process, as previously mentioned, involves the application of high temperatures and pressure, whereas in catalytic cracking the oil is heated to a lower temperature and pressure where little or no thermal cracking occurs. The vapors are intimately in contact with the surface of a catalyst, where the oil molecules are broken into smaller aggregates and rearranged to produce high yields of motor fuels having exceptionally high octane numbers.

The modern "fluid" catalytic cracking processes[4] employ a finely divided solid catalyst made by aerating the ground powder of an alumina-silica gel. This is maintained at all times as a simulated fluid by suspension in the reacting vapors or in the regenerating air. A high degree of turbulence is necessary throughout the system to ensure a uniform suspension. Under these conditions the solid catalyst flows similarly to a liquid and exerts a like pressure. Because of the even distribution of the catalyst and because of its high specific heat in relation to the vapors reacting, the entire cracking reaction can be maintained at a remarkably exact temperature. Separation of the catalyst from gases or vapors after the reaction and regeneration processes is largely by means of cyclone separators. Coke and tar are formed on the catalyst by the cracking.

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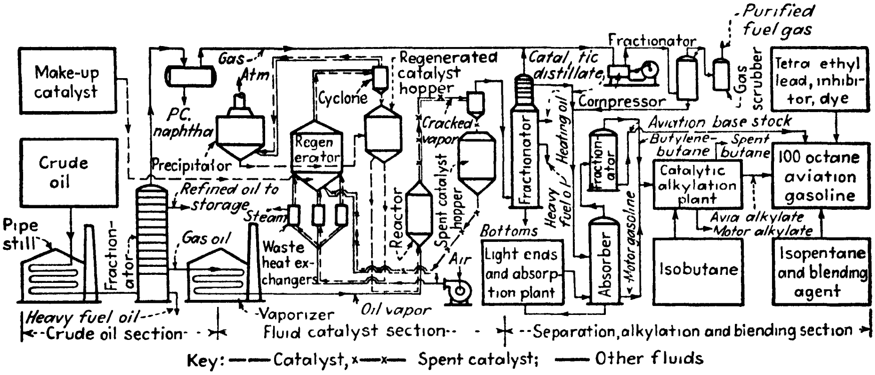
[1] NELSON, *op. cit.*, p. 29, presents a tabulation of the gasoline yields from many domestic crudes; FAUST, What Takes Place in Thermal Cracking, *Petroleum Refiner*, **22,** 45 (1943) describes reactions.

[2] KRAEMER and THORNE, Petroleum Investigation, U.S. Congress, House of Representatives, Hearing on H. R. 290 and H. R. 7372, 76th Congress, 1939; EGLOFF, NELSON, and MORRELL, Motor Fuel from Oil Cracking, *Ind. Eng. Chem.*, **29,** 1555 (1937).

[3] PRICKETT and NEWTON, Recent Developments in Houdry Fixed Bed Catalytic Processes, *Petroleum Refiner*, **22,** No. 11, 107 (1943); BATES, ROSE, KURTZ, and MILLS, Composition of Catalytically Cracked Gasolines, *Ind. Eng. Chem.*, **34,** 147 (1942); *cf.* GROSSE, Concept of Catalytic Chemistry, *Ind. Eng. Chem.*, **35,** 762 (1943): THOMAS, *et. al.*, Cracking with Catalysts, *Petroleum Refiner*, **22,** No. 11, 95 (1943).

[4] MURPHREE, *op. cit.*, pp. 627–630, flow sheets and descriptions of fluid catalytic cracking processes are presented; MURPHREE, BROWN, FISCHER, GOHR, and SWEENEY, Fluid Catalyst Process, *Ind. Eng. Chem.*, **35,** 768 (1943), flow sheets and description; RUSSELL, Genesis of a Giant, *Petroleum Refiner*, **23,** No. 1, 91 (1944).



Raw materials	Amount	Use	Products	Amount
Heavy gas oil.	100 bbl.	Power for air	Aviation gasoline	78.4 bbl.
Virgin naphtha	21.5 bbl.	Heat for furnace	Motor gasoline	6.6 bbl.
Butane	9.7 bbl.		Light fuel oils	35.0 bbl.
Tetraethyl lead.. ..	3.8 gal.			

FIG. 8.—Flow diagram for making 100 octane aviation gasoline by fluid catalytic cracking. The volatilized gas oil meets continuously a flowing stream of the regenerated catalyst and proceeds into the reactor chamber where the cracking takes place. The mixture of the catalyst and the cracked vapors passes overhead to cyclones that separate the catalyst from the petroleum vapors that in turn pass overhead to a product fractionator. The spent-coked catalyst flows down a standpipe where air carries it up (air lift) to the large regenerator chamber where the coke is burned off. The flue gases and the catalyst pass overhead through cyclones for the separation of most of the catalyst from the flue gases and finally through a Cottrell electrical precipitator before the flue gases are discharged through the stack. Some of the catalyst in the regenerator system is recirculated through heat exchangers underneath for making steam. There are no valves in the above outlined continuous circulation. (*Courtesy of Standard Oil Company of New Jersey.*)

These are burned from the catalyst with air during the regeneration part of the cycle. Both cracking and regenerative cycles are continuous.

The fluid catalytic cracking process has been put into operation by the Standard Oil Company of New Jersey on a very large scale with plants at Baton Rouge and near Baltimore. This procedure operates at a pressure of about 2 lb. gage and at a temperature of from 700 to 1000°F. It produces a high-octane motor fuel, very suitable for blending into aviation gasoline. This fluid catalytic cracking is illustrated[1] by the flow diagram of Fig. 8 and the picture of Fig. 9. The latest equipment for the commercialization of this "cat" cracking is the so-called *Baltimore giant* of the Standard Oil Company of New Jersey, which cost $14,000,000, has more than 100 miles of pipe lines, and is 253 ft. high. The flow diagram of Fig. 8 includes the cracking or pyrolysis under the control of the fluid catalyst of the gas oil and also of the making of an alkylate from the butylenes also formed, reacting with added isobutane.

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[1] For a pictured flow sheet, see *Chem. & Met. Eng.*, **50**, No. 12, 130 (1943).

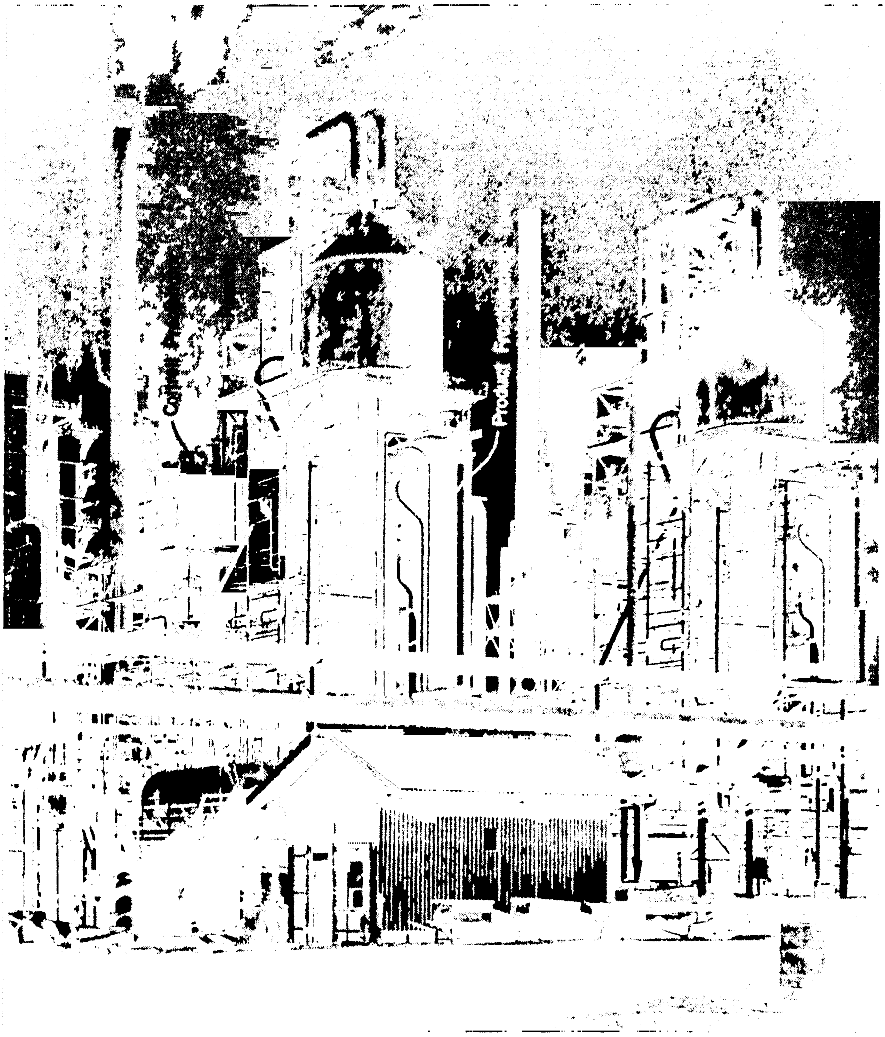
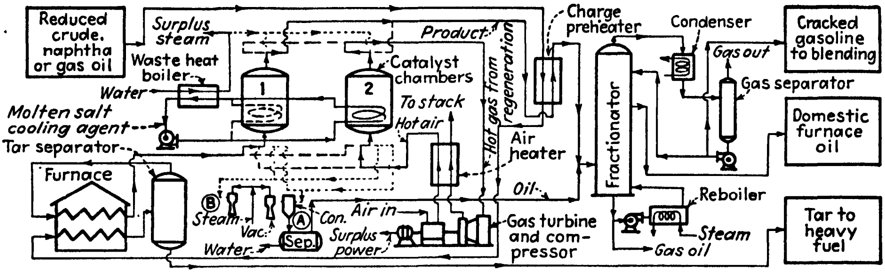


FIG 9.—Two "cat" crackers at Baton Rouge (*Courtesy of Standard Oil Company of New Jersey*)

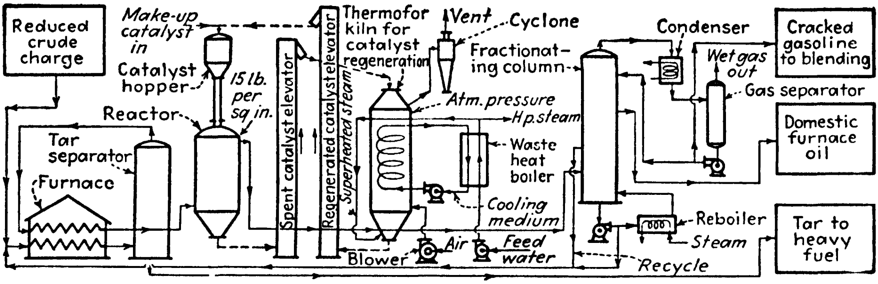
This fluid catalytic process gives promise of contributing a valuable principle to the chemical industry. The use of a large amount of turbulent solid capable of absorbing much heat in the reaction mass greatly aids in the elimination of temperature variations and hot spots. If no catalytic action is desired, an inert, powdered solid[1] may be used.



Notes and Key: Three catalyst chambers used instead of two as shown. No. 1 is shown on run and No. 2 being regenerated by burning off coke with compressed hot air. Dashed lines indicate open connections during phase shown. Dotted lines show purge connections. Ⓐ is system for purging oil vapor from chambers prior to regeneration. Ⓑ is system for purging waste gas from chambers after regeneration.

FIG. 10.—Flow sheet for catalytic cracking—Houdry process.

Two other catalytic cracking[2] processes should be mentioned: the *Houdry* (see Fig. 10), using a fixed base catalyst and the *Thermofor catalytic cracking* (T.C.C.) (Fig. 11), employing a flowing bead-type catalyst. The catalysts are aluminum silicates, either clay or artificial.



Key: —→——, Clay type or bead catalyst; ———, Other flow lines

FIG. 11.—Flow sheet for catalytic cracking—Thermofor process.

Both produce high-quality aviation gasoline base stock for blending with alkylate, toluene, or cumene to aviation gasoline. The Thermofor units are economical in small sizes (1,000 bbl. per day). In many instances where the Thermofor units are installed for first-pass cracking to produce butylenes and gasoline, this gasoline is recracked over Houdry units for producing final aviation or high-octane base stock.

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[1] This principle may be applied to the control of organic oxidations that are inclined to proceed to where the oxidation is a combustion.

[2] *Bull.* R-8, Lummus Company, New York, 1944, flow chart, descriptions, and pictures; both are licensed by Houdry Process Corp. VAN ANTWERPEN, Thermofor Catalytic Cracking, *Ind. Eng. Chem.*, **36**, 694 (1944).

Figure 12 shows the *Universal Oil Products thermal cracking* process. The charging stock is topped crude (crude from which the lighter fractions down to gas oil have been removed by distillation. See Fig. 3). The topped crude is charged to a fractionating tower which is heated by vapors from the flash tower. The lighter part of the charge is thus vaporized but not enough heat is present to carry it out of the top of the column. These vapors of light oil are condensed above the trap tray and are sent to the heating furnace. The heavy oil fraction of the charge is removed from the bottom of the tower and also sent to the heating furnace.

The furnace has two coils: one to heat the light oil and the other to heat the heavy oil. The heavy oil is easier to crack but, because it has not been vaporized, it contains tars and other materials that tend to form coke and clog the furnace. Thus the heavy-oil coil of the furnace is not operated at so high a temperature as the light-oil coil and it is so constructed as to permit easier cleaning.

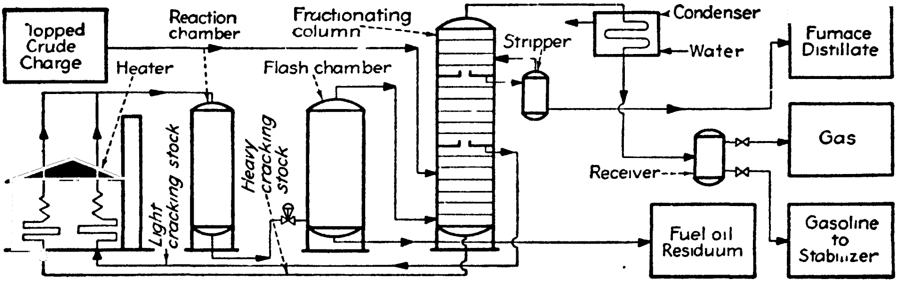


FIG. 12.—Universal Oil Products two-coil selective cracking unit.

The heated and partly cracked material from both coils is combined and sent to a reaction chamber for the completion of the cracking or pyrolysis. This is simply a large tower and most of the coke produced by the cracking operation is deposited in it. Several chambers are used in practice, though Fig. 12 shows only one. When a chamber becomes filled with coke, the heated material is sent from the furnace to another tower while the first one is being cleaned.

The cracked material, which has lost most of its coke, is piped to the flash chamber where the pressure is reduced. This reduction in pressure causes the lighter portions to vaporize from the residuum which is removed at the bottom. The vapors next flow to the bottom of the fractionating tower where their heat is used to separate the charging stock. The vapors that reach the top of the column are condensed and consist of gasoline containing dissolved gas. Part of the vapor is heavier than gasoline and condenses near the top of the column. This is called *furnace distillate*. Any material too heavy to reach either of these levels in the column is sent back to the cracking furnace.

Reforming.—Reforming involves both cracking and isomerization. Straight-run gasoline and light naphthas usually have very low octane numbers. By sending these fractions to a reforming unit and giving them a light "crack" their octane number may be increased. This upgrading is probably due primarily to isomerization (conversion of straight-chain compounds to branched-chain compounds), but some cracking also

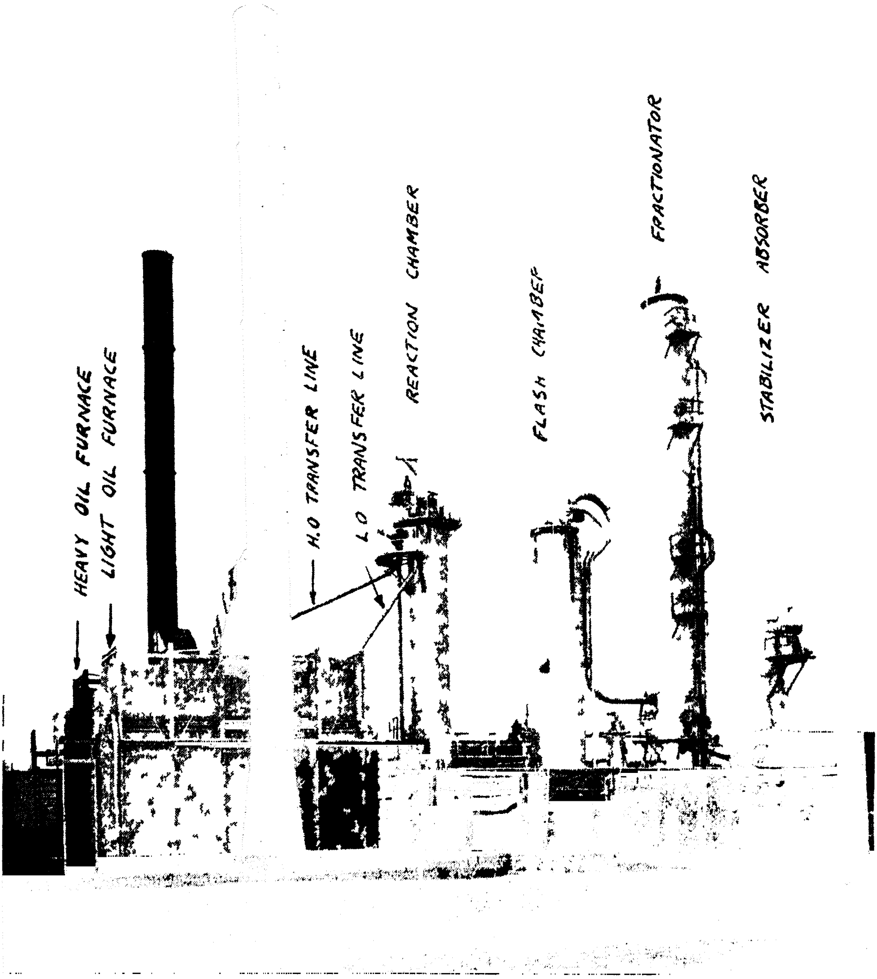
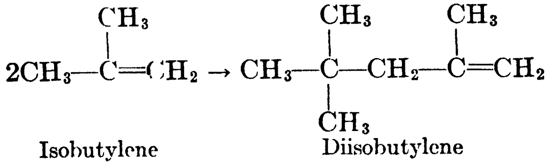


FIG. 13.—Universal Oil Products two-coil selective cracking unit.

occurs as shown by the decrease in the quantity of material of the desired boiling range obtained.

Polymerization.—Rapid progress has been made in the development of polymerization processes for converting by-product hydrocarbon gases produced in cracking into liquid hydrocarbons suitable for use as high-octane motor and aviation fuels. To combine gases or highly volatile liquids by polymerization to form heavier fractions, the combining fractions must be unsaturated. The hydrocarbon gases from cracking stills, particularly the olefins, have been the foundation of polymerization. The following equation is typical of polymerization reactions. Propylene and isobutylene are the olefins usually in the cracked stock, although ethylene and some higher olefins are also present.



$$2CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 \rightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{C}=CH_2$$

Isobutylene Diisobutylene

Vapor-phase cracking produces considerable quantities of unsaturated gases; hence polymerization units are often operated in conjunction with this type of cracking. *Thermal* polymerization is practical only for large-scale operations because of the difficulty of obtaining good heat control in small-sized units, whereas *catalytic* polymerization is practical on both a large and a small scale and is furthermore adaptable to combination with reforming to increase the quality of the gasoline (see Fig. 14).

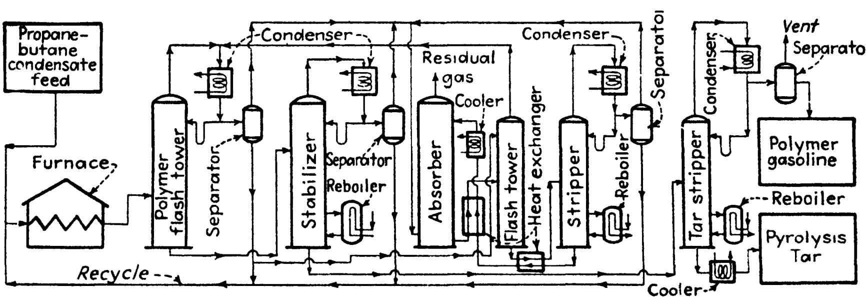


FIG. 14.—Flow sheet for polymer gasoline—Pure Oil thermal process.

Figure 15 shows the essential steps in a catalytic polymerization process, which is quite simple and consists of passing the preheated unsaturated gases through towers containing the granular catalyst in beds. A catalyst frequently employed is a "solid phosphoric acid," *i.e.*, a silicophosphate, with which yields of 100 gal. or more of polymer gasoline are obtained per pound of catalyst. Until recently the catalyst had to be regenerated at frequent intervals by burning off the carbonaceous deposits, but new developments have greatly increased the active life of the catalyst and now regeneration is seldom necessary.

Alkylation.—Alkylation processes are fundamentally similar to polymerization but differ in that only part of the charging stock need be unsaturated. Figure 16 shows two simplified alkylation processes. The reactions are given under Unit Processes (page 819). In practice the reactions are considerably more complex. The molecule may break down into fragments which then recombine to form a new molecule. Another secondary reaction is isomerization. The tertiary carbon atom of the isobutane is quite reactive and is the basis of the alkylation.

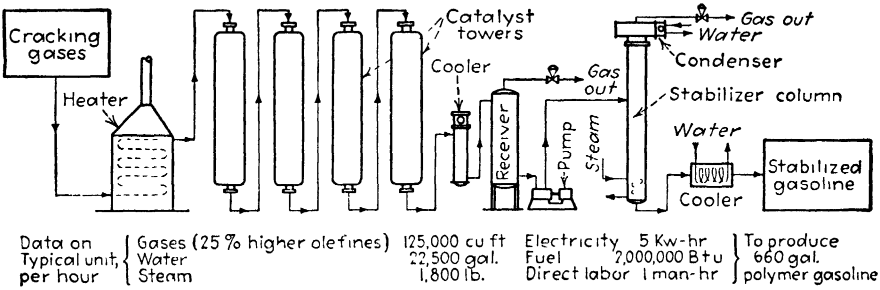


FIG. 15.—Polymerization gasoline—Universal Oil Products catalytic process.

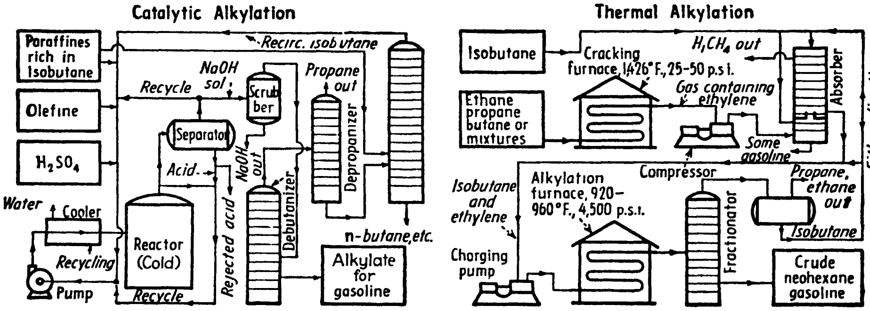


FIG. 16.—Flow sheet for gasoline by alkylation.

The cold catalytic process[1] employs 98 per cent sulfuric acid as the catalyst. The charging gas stock consists of two parts: paraffins rich in isobutane, and olefins. The isobutane is separated from the other paraffins in a fractionating tower and sent, together with the olefins and catalyst, to the cold reactor. The isobutane is employed in large excess to prevent olefins from reacting with themselves. The products from the reactor are sent to a separator. The acid layer is removed from the bottom. Part of it is discarded to prevent catalyst contamination, and part is fortified with fresh acid and recycled. The hydrocarbon layer is removed from the top of the separator, scrubbed with caustic solution to remove any last traces of acid, and sent to a debutanizing tower. The butanes and the propane are taken off the top and fractionated again in another tower (depropanizer) to remove the propane, and the butanes finally are isomerized with the charging stock paraffins to produce more isobutane. "Alkylate" for blending into aviation gasoline is removed near the bottom of the debutanizer.

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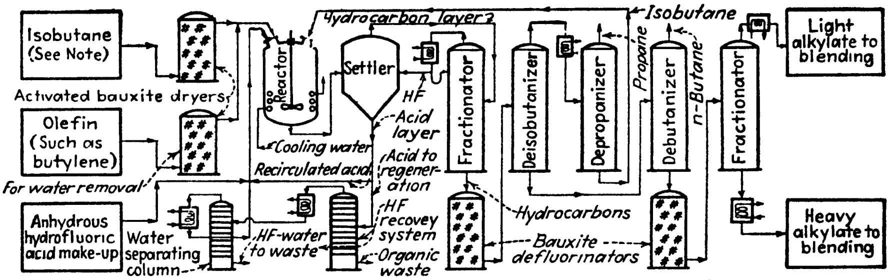
[1] ANON., Alkylation by Catalysis, *Chem. & Met. Eng.*, **49**, No. 10, 108 (1942); KENNY, Problems in Alkylation Plant Operation, *Petroleum Refiner* **21**, No. 7, 193 (1942).

Recently alkylation with liquid hydrogen fluoride[1] has been put into practice (see Fig. 17). Here the acid can be used repeatedly and offers no acid disposal problem. The temperature range is also more cheaply maintained as no refrigeration is necessary, being from 105 to 115°F.



Note· See Flow Sheet Fig. 18 for isomerization process for isobutane from n-butane

FIG. 17.—Flow sheet for gasoline by alkylation—hydrofluoric acid catalytic process.

The reaction is as given under the unit process of alkylation (page 819) with a several-fold excess of isobutane over the butylene to minimize realkylation of the primary alkylate. The anhydrous hydrofluoric acid, when dirty, is easily regenerated by distillation. Sufficient pressure is required on the system to keep the reactants in the liquid phase. Corrosion is low.

Thermal alkylation[2] is also shown in Fig. 16. The olefin usually reacted is ethylene which is obtained by cracking mixtures of ethane, propane, and butanes. The gas from the cracking furnace, containing ethylene, methane, hydrogen, and a little gasoline, is compressed and sent to the absorber. The gasoline is condensed and removed at the bottom. The gases are mixed with isobutane which selectively absorbs the ethylene. The methane and hydrogen pass out at the top, and the mixture of isobutane and ethylene is pumped to the alkylation furnace.

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[1] FREY, Commercial Alkylation with Hydrogen Fluoride Catalyst, *Chem. & Met. Eng.*, **50**, No. 11, 126 (1943), picture and flow diagram; GERHOLD, IVERSON, NEBECK, and NEWMAN, "The Development of the Hydrogen Fluoride Alkylation Process," Booklet 253, Universal Oil Products Co., Chicago, 1943.

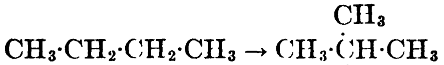
[2] EGLOFF on p. 563 of "Rogers' Manual of Industrial Chemistry."

Fractionation separates the alkylation products into crude neohexane gasoline and propane, ethane, and isobutane. The isobutane is recycled.

Hydrogenation.—Hydrogen is added to an unsaturated hydrocarbon under high pressure and temperature in the presence of a catalyst to produce a more fully saturated product. Exceedingly high yields of gasoline or of lubricating oils with a high viscosity index, low carbon residue, and high resistance to oxidation can be obtained by hydrogenating heavy oils. The entire result is an upgrading of the products. The adoption of hydrogenation has not been too general owing to high initial cost of plant and equipment,[1] but it is economical and very useful in specialized procedures. It will be employed more and more in the future though probably not for lubricating oils, which are being manufactured more suitably by solvent extraction. The diisobutylene obtained by polymerization of isobutylene is frequently hydrogenated to secure a more suitable aviation blending agent. The Bergius process, originated in Germany, for the production of oils by hydrogenation of coal finds extensive use in Europe, where petroleum is unavailable or very expensive and coal is cheap. It has been tried in this country only on a semiworks scale. The synthesis of a motor fuel from carbon monoxide and hydrogen is a hydrogenation process which has been industrialized in Germany as the Fischer-Tropsch process[2] to make Synthol. It is not expected that this process will be economical in America for many years.

Chlorination.—Both olefins and paraffins may be chlorinated to yield valuable products. Ethylene dichloride, prepared by the reaction of ethylene and chlorine, is used in conjunction with tetraethyl lead in "ethyl" gasoline. Ethyl chloride is important as the raw material in the manufacture of tetraethyl lead. Chloro-pentanes are the basis for the Sharples process for synthetic amyl alcohols.

Isomerization.[3]—This unit process has become of the utmost importance to furnish the isobutane need for making "alkylate" as a basis for aviation gasoline (see Alkylation, page 828). The reaction may be formulated:



$$\underset{n\text{-Butane}}{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3} \rightarrow \underset{\text{Isobutane}}{CH_3{\cdot}\overset{CH_3}{\overset{|}{C}}H{\cdot}CH_3}$$

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[1] MURPHREE, BROWN, and GOHR, Hydrogenation of Petroleum, *Ind. Eng. Chem.*, **32,** 1203 (1940); **31,** 1083 (1939).

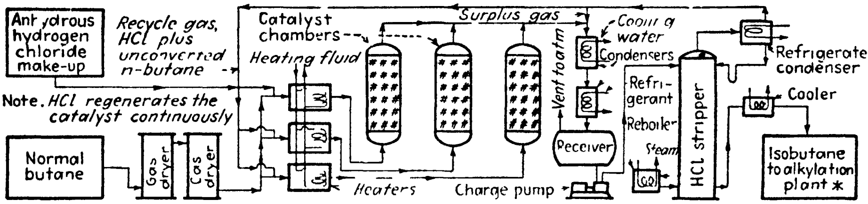
[2] FISCHER, ROELEN, and FEIST, Synthesis of Gasoline by the Fischer-Tropsch Process, *Petroleum Refiner*, **22,** No. 12, 97 (1943); **23,** No. 2, 112 (1944). This presents a good review with many references.

[3] EGLOFF, HULLA, and KOMAREWSKY, "Isomerization of Pure Hydrocarbons," Reinhold Publishing Corporation, New York, 1942; ANON., Liquid-phase Isomerization, *Petroleum Refiner*, **23,** No. 2, 61 (1944).

This equilibrium reaction is accelerated by $AlCl_3$ promoted by HCl, both in the anhydrous form. At 250°F. and under about 300 lb. pressure, a conversion of 45 to 55 per cent is attained commercially. Ninety-eight per cent of the butane charged is recovered as such or as isobutane. Being in the anhydrous state, the reaction can be carried out in steel equipment. The tertiary carbon atom formed by the isomerization is very reactive (see Fig. 18).

Hydration to Alcohols.[1]—When ethylene is passed into concentrated sulfuric acid, the latter retains the hydrocarbon as the ester, ethyl sulfuric acid, which by dilution and heat can be hydrolyzed to ethyl alcohol. The alcohol may then be distilled off and the acid concentrated and reused.

$$C_2H_4 + H_2SO_4 \rightarrow C_2H_5HSO_4$$
$$C_2H_5HSO_4 + H_2O \rightarrow C_2H_5OH + H_2SO_4$$



* Product contains some n-butane which is normally segregated in distillation section of the alkylation plant and returned for further isomerization

Fig. 18.—Flow sheet for isomerization of butane—Shell catalytic process.

Virtually all the isopropyl alcohol used is made in this fashion from propylene. Recently the catalytic hydration of ethylene in the vapor phase has become of increasing significance.

Hydroforming or Aromatization.—Aromatization may be linked with cyclization and is accompanied by much coke formation on the catalyst. If carried out under partial hydrogen pressure, this coke making is much decreased. This process involving catalytic dehydrogenation in presence of hydrogen is known as *hydroforming*. The reactions given under this subhead under Unit Processes (page 820) are probably more complicated with methylcyclohexane being formed before toluene. This process has been of vital importance during the Second World War for the making of toluene for explosives, a very large amount being produced in this fashion.[2] It is carried out at 1000°F. and with good yields (see Figs. 19 and 20). Benzene and other aromatics are also being made.

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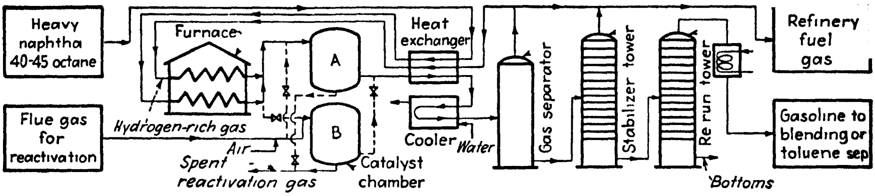
[1] "Science of Petroleum," p. 2803; ANON., Spirit of the Times, *Petroleum Refiner* **23**, No. 1, 101 (1944), pictured flow diagram.

[2] SMITH and MOORE, Hydroforming; A New Refining Process, *Chem. & Met. Eng.*, **48**, No. 4, 77 (1941); TRUSTY, Petroleum as a Source of the Aromatic Hydrocarbons, *Petroleum Refiner*, **22**, No. 4, 95 (1943); MURPHREE, *op. cit.*, p. 625, flow sheet.

Oxidation.[1]—The oxidation reaction in petroleum gives more troubles than useful products, forming as it does gums and resins that interfere with the employment of gasolines, particularly those that contain unsaturated bodies. However, some serviceable products are obtained from petroleum by oxidation, *e.g.*, formaldehyde by restricted oxidation of natural gas. Much study is also being directed toward making fatty acids[2] from paraffins.



Notes Catalyst chambers A and B are operated alternately to permit regeneration of one. A is shown on the line with B regenerating This process produces a high-aromatic gasoline of up to 80 oct and may be operated to produce a high toluene yield

FIG. 19.—Flow sheet for hydroforming to high-octane gasoline and toluene.

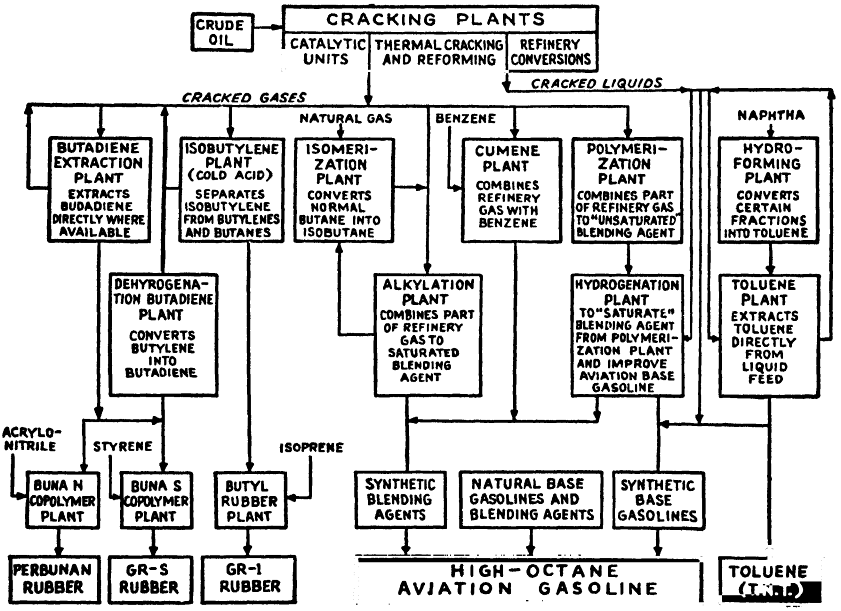

CRUDE OIL
CRACKING PLANTS
CATALYTIC UNITS
THERMAL CRACKING AND REFORMING
REFINERY CONVERSIONS
CRACKED GASES
CRACKED LIQUIDS
NATURAL GAS
BENZENE
NAPHTHA
BUTADIENE EXTRACTION PLANT EXTRACTS BUDADIENE DIRECTLY WHERE AVAILABLE
ISOBUTYLENE PLANT (COLD ACID) SEPARATES ISOBUTYLENE FROM BUTYLENES AND BUTANES
ISOMERIZATION PLANT CONVERTS NORMAL BUTANE INTO ISOBUTANE
CUMENE PLANT COMBINES REFINERY GAS WITH BENZENE
POLYMERIZATION PLANT COMBINES PART OF REFINERY GAS TO "UNSATURATED" BLENDING AGENT
HYDROFORMING PLANT CONVERTS CERTAIN FRACTIONS INTO TOLUENE
DEHYROGENATION BUTADIENE PLANT CONVERTS BUTYLENE INTO BUTADIENE
ALKYLATION PLANT COMBINES PART OF REFINERY GAS TO SATURATED BLENDING AGENT
HYDROGENATION PLANT TO "SATURATE" BLENDING AGENT FROM POLYMERIZATION PLANT AND IMPROVE AVIATION BASE GASOLINE
TOLUENE PLANT EXTRACTS TOLUENE DIRECTLY FROM LIQUID FEED
ACRYLONITRILE
STYRENE
ISOPRENE
BUNA N COPOLYMER PLANT
BUNA S COPOLYMER PLANT
BUTYL RUBBER PLANT
SYNTHETIC BLENDING AGENTS
NATURAL BASE GASOLINES AND BLENDING AGENTS
SYNTHETIC BASE GASOLINES
PERBUNAN RUBBER
GR-S RUBBER
GR-1 RUBBER
HIGH-OCTANE AVIATION GASOLINE
TOLUENE (T.N.T.)

FIG. 20.—Simplified flow sheet showing derivation of the three most important war products from petroleum. (*Courtesy of Standard Oil of Louisiana.*)

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[1] GRUSE and STEVENS, *op. cit.*, pp. 119–138, 653.

[2] PARDUN and KUCHINKA, Reaction Rates in the Liquid-phase Oxidation of Paraffins, *Petroleum Refiner*, **22**, No. 11, 140 (1943).

The petroleum industry's contribution to the Second World War is large and most important. The products are summarized in outline form by the simplified flow diagram of Fig. 20. Aviation gasoline is manufactured by a number of different processes as outlined on this flow chart. Here is also shown the basic position of petroleum in the wartime rubber projects, more fully described in Chap. XXXVI.

* * * * * *

Chemical Treatment.—Some type of chemical treatment to remove or alter the constitution of impurities in petroleum products is usually necessary to produce marketable material.[1] Depending upon the particular treatment used, one or more of the following purposes are achieved:

1. Improvement of color.
2. Improvement of odor.
3. Removal of sulfur.
4. Removal of gums.
5. Improvement of stability to light and air.

Strong sulfuric acid is widely used to produce water-white products but it has the great disadvantage of also dissolving or reacting with valuable olefins. (See Fig. 3 of Chap. XIX for recovery of sulfuric acid from the spent sludge acid.) With the public acceptance of colored (dyed) products the necessity of color improvement is disappearing.

Several processes are available for the alteration of objectionable sulfur and the consequent improvement in odor.[2] The *doctor treatment* is probably used more extensively than any other. This process consists of agitating the oil with an alkaline solution of sodium plumbite and a small amount of sulfur. The sulfur compounds usually found in oils are mercaptans. These give the material a disagreeable odor and cause corrosion. *Doctor* converts mercaptans to lead sulfide and comparatively harmless disulfides.

$$2RSH + Na_2PbO_2 \rightarrow (RS)_2Pb + 2NaOH$$
$$(RS)_2Pb + S \rightarrow R_2S_2 + PbS$$

Catalytic methods for desulfurization are modern developments and are becoming increasingly important.

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[1] MASON, BENT, and MCCULLOUGH, Naphtha Treating "Pays Its Way," *Petroleum Refiner*, **20**, 432, (1941). For a fundamental presentation of this subject, see Chap. 8 in Gruse and Stevens, *op. cit.*

[2] HAPPEL, CAULEY, and KELLY, Critical Analysis of Sweetening Processes and Mercaptan Removal, *Petroleum Refiner*, **21**, 406 (1942); RYAN, Influence of Sulfur Compounds on Octane Number and Lead Susceptibility of Gasoline, *Ind. Eng. Chem.*, **34**, 824 (1942); NELSON, *op. cit.*, pp. 582*ff*.

It is now common practice to add antioxidants[1] to prevent formation of gums rather than to remove them chemically. Among the antigumming materials used are α-naphthol, substituted catechols, cresols, benzyl-*p*-aminophenols, and certain wood-tar and coal-tar fractions.

Research.—The petroleum industry has been characterized by continuous improvement based upon research[2] and a willingness to replace antiquated equipment or old processes by more modern ones. This development went through two phases—the first, wherein the *unit operations* of distillation, heat transfer, fluid flow, and the like, were subjected to accurate study and experimentation, resulting in the carrying through of these operations with greater efficiency and consequently less cost. Investigations of these unit operations are naturally being continued. However, the second phase[3] of research in this field applies to the study of chemical changes involving petroleum raw materials or petroleum products. The industrial application of these we recognize as *unit processes.* We are right in the midst of this aspect of the development of the petroleum industry. It has yielded rich returns and is certain to yield even more products of greater usefulness in the future. The long-term competitive approach to synthetic rubber lies in this field.

No longer can petroleum companies be satisfied simply to separate into salable fractions the various products as they occur in petroleum. To maintain a competitive and well-rounded position many petroleum compounds must be altered to obtain products of greater usefulness or value. Each year is showing a higher percentage of petroleum sales arising from the action of chemical change on petroleum raw materials. Indeed the petroleum industry is fast becoming one of the most important sources for cheap raw materials for the chemical industry. Such chemical change will be more marked in the future than it has been in the past.

The present sound technical position has all come about through the wise dependence of the petroleum executives upon research in the very broadest meaning of this term, *protected by patents covering the public disclosure of new discoveries.* It is estimated by the U.S. Bureau of Mines that the petroleum industry is spending about $20,000,000 annually on its research program, employing therein about 6,000 people. This is to be compared with about 1,000 such employees in 1927. It is also to be compared with about 50,000 research workers engaged in all the industries in the United States. Such a program gives rich promise for the future.

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[1] GRUSE and STEVENS, *op. cit.*, p. 132.

[2] BROOKS, Petroleum Research and Wars, *Ind. Eng. Chem.*, **34**, 798 (1942); FITZGERALD, Mobilizing Petroleum Hydrocarbons, *Chem. & Met. Eng.*, **49**, No. 3, 83 (1942).

[3] Many divide petroleum development into three phases: the first pertaining largely to the physical operation of distillation, the second characterized by cracking, and the third distinguished by the many other chemical processes or reactions that are being applied industrially in this field.

Problems

1. A certain gasoline has an A.P.I. gravity of 62° at 60°F./60°F. What is its specific gravity? What is its gravity in degrees Baumé? How much will a 50-gal. barrel of it weigh?

2. Gasoline is sweetened to remove odor. The primary reaction involved may be assumed to be

$$2RSH + (O) \rightarrow RSSR + H_2O$$

If a straight-run gasoline (A.P.I. gravity = 51.2° at 60°F./60°F.), containing 0.06 per cent sulfur all of which is assumed to be present as mercaptans, could be sweetened catalytically by the use of the cheapest known oxidizing agent, air, how many cubic feet of dry air at 60°F. would be required to sweeten 1,000 bbl. (42 gal. each) of this gasoline if 60 per cent of the oxygen fed took part in the reaction?

3. A gas has the following composition by volume: H_2, 5.4 per cent; CH_4, 9.9 per cent; C_2H_6, 6.1 per cent; C_3H_8, 26.9 per cent; C_4H_{10}, 51.7 per cent. If this gas is compressed to 60 lb. per sq. in., how many pounds per hour will pass through an 8-in. inside diameter pipe line if the gas flows at a temperature of 60°F. and a velocity of 6 ft. per sec.?

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CHAPTER XXXVIII

INTERMEDIATES, DYES, AND THEIR APPLICATION

Coal has been called the *black diamond.* The analogy obtains not only because both consist of carbon but because from both we get a rainbow of colors, one from the effect of light and the other from the action of various chemicals. The purpose of this chapter is to follow through the manifold chemical and engineering changes that transform coal by the action of many other chemicals into literally a coat of a thousand hues. The 1,000-odd commercial dyes that we use bring grace and variety in what would otherwise be a drab world. Furthermore, the entire dye industry throws a protective mantle over many another industry and even over a wise scheme of national preparedness.

Because of the way in which dyes are connected with or enter into so many other phases of our industrial life we have learned to view the industry as an essential one. It took the First World War to convince America and some other nations of this fact. Prior to 1914, Germany made a very large proportion of the dyes used throughout the world; indeed, propaganda insisted that only on the banks of the Rhine could dyes be made economically and of a high quality. However, since the derangement of industrial life by the cutting off of German dyes beginning in 1914 and since the realization of the connection between the raw materials of the dye industry and a wise program of national preparedness, many of the important nations have endeavored to build up within their own borders and from their own basic materials a self-contained dye industry. If we run our mind's eye across a portion of our industrial life, we shall see how the dyes enter in. Consider clothing, drapes and wall coverings, paints and varnishes, and many other industries. In these, dyes act to make a great many products salable. We *could* go around in gray homespun, live in unpainted houses, and keep the sun out with unbleached or undyed curtains, but much of the attractiveness of our modern civilization would disappear. We would live literally in a colorless world. Table 1 presents a summary for many of the industries into which dyes enter as an essential constituent. One dollar's worth of dyes makes salable about $100 worth of other products. Our $60,000,000 or $70,000,000 worth of dyes help mightily in the disposal of about 6 billion dollars' worth of other products entering into our modern technical civilization! The table shows also that over 1,500,000

TABLE 1.—INDUSTRIES DIRECTLY DEPENDENT ON DYES

Industry	Establishments			People employed			Capital invested, in thousands	Value of products, in thousands		
	1914	1937	1939	1914	1937	1939	1914	1914	1937	1939
Dyeing and finishing textiles....	507	533	580	48,467	74,982	63,048	$139,194	$109,292	$283,262	$294,850
Cotton textiles............	1,287	1,237	1,248	385,964	435,428	409,317	678,809	688,094	1,274,295	1,168,171
Hosiery and knit goods.......	1,622	1,821	2,089	150,520	231,064	236,628	215,826	258,913	659,974	714,429
Silk goods..................	902	423	350	108,170	45,986	35,724	210,072	254,011	132,298	113,826
Woolen and worsted goods.....	799	508	583	158,692	132,158	140,022	399,653	379,484	697,590	685,312
Rayon.....................	.....	425	479	....	70,853	84,097	....	....	272,437	328,074
Felt goods and wool felt hats....	83	53	49	5,284	7,749	7,767	22,893	15,638	45,122	39,584
Carpets and rugs..............	97	71	61	31,309	33,941	28,727	85,154	69,128	182,228	160,320
Linen goods.................	21	12	9	3,567	1,862	1,613	8,810	6,960	6,441	5,695
Fur felt hats................	224	140	158	21,318	15,926	14,515	39,401	37,350	66,775	63,578
Leathers....................	741	2,962	3,062	55,936	281,268	280,411	332,180	367,202	1,096,490	1,043,076
Paints and varnishes..........	800	1,124	1,255	16,083	31,664	28,173	129,534	145,624	538,461	528,847
Printing inks..............	70	184	206	1,391	2,793	2,572	11,943	13,830	47,347	49,132
Paper (paper alone)........	495	647	638	42,481	110,809	110,575	177,413	158,427	957,940	933,016
Blacking and stains^a....	197	147	.....	1,766	1,536	....	4,986	9,882	19,183	
Bluing................	66	14	13	254	67	55	712	1,184	1,129	1,142
Perfumes and cosmetics.....	496	478	539	2,897	10,158	10,363	9,647	16,899	132,136	147,466
Writing inks............	54	17	15	512	366	254	2,464	2,784	3,476	2,951
Artificial flowers^b.......	217	189	314^b	4,808	5,657	6,650	3,349	7,614	14,378	18,504
Buttons...............	517	291	316	14,511	12,026	10,972	19,075	20,712	31,291	29,817
Feathers and plumes^b.....	239	61	^{b}	4,483	559	....	5,396	11,451	2,320	
Fur goods..................	1,322	1,642	2,175	9,030	12,952	13,111	29,677	43,633	155,605	168,032
Hair work..................	205	35	42	1,193	434	322	2,543	3,335	2,449	1,401
Totals..................	.....	.....	.....	....	....	....	....	2,621,447	6,728,127	6,497,223

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[a] Included in Paints and Varnishes in 1939.

[b] Combined in 1939.

employees earn their livelihood in these various industries. Therefore, in evaluating our dye industry we should not look upon it as simply the making of the dyes themselves, but we should follow through the many paths the dyes take to the consumers' goods.

This is not the whole story. The First World War demonstrated how closely the chemical industry and, in particular, the dye industry were connected with the system of national preparedness. The raw materials, which in times of peace enter into the making of intermediates that are changed into dyes, in many instances are the basis of our high explosives in time of war. This is true of benzene and toluene which furnish dyes or such explosives as picric acid, tetryl, and T.N.T. Likewise the acids that are used in times of peace to make dyes are absolutely essential to make the nitro-derivatives which are such an important division of explosives. And finally, much of the plant and many of the trained personnel who in times of peace make dyes, are being transferred in the present dire emergency to the making of explosives or to serve as the nucleus for rapid expansion of such materials.

In 1914 we imported 90 per cent of our dyes. Our position then could be represented as in the accompanying table.

SUMMARY OF DYES, 1914

	Employees	Firms manufacturing	Pounds
Dyes made	528	7	6,619,729
Dyes imported	...	..	45,950,895

This does not represent the real picture for, while not belittling the excellent work that the 7 American firms accomplished, it is a fact that many of the necessary intermediates were being imported from Germany, Switzerland, or even from England. The dye industry had been struggling for 50 years to establish itself here in the United States. That grand old man of chemistry, the late Dr. Ellwood Hendrick, related that in his youth he had run a dye factory located up the Hudson River in New York until German competition forced the turning over of the plant to the sheriff in the year 1885. Other equally courageous souls had tried to break in and a few succeeded. When importations were stopped in the summer of 1914, the country became panicky over the dye shortage. The dark corners of warehouses were searched for abandoned kegs of dyes; even the floors were scraped and extracted. Simultaneously, the chemical industry took up the challenge.

Thanks to the skill of American chemists, the versatility of American engineers, and the confidence of American businessmen, the establishment of a permanent dye industry in America rapidly took shape. Indeed, before the ending of the war in 1918, a good start had been made. The country had learned its lesson and both parties in Congress supported a wise temporary tariff to encourage the further development leading to the independence of America in dyes and intermediates. In 1920 the country *was* independent; the scales had been reversed; America was then manufacturing over 90 per cent of the dyes needed for domestic consumption out of American intermediates and American raw materials. This accomplishment was not the complete story for, although some products were still being imported, certain largely consumed dyes, as sulfur black and indigo, were being made on such a large scale and so cheaply that they entered world markets in competition with products made in Ger-

TABLE 2.—INTERMEDIATES, DYES, AND CERTAIN OTHER CLASSES OF COAL-TAR CHEMICALS: COMPARISON OF UNITED STATES PRODUCTION AND SALES, AVERAGE 1934–1938, ANNUALLY 1939 AND 1940[a]
(Production and sales in thousands of pounds; sales value in thousands of dollars)

Product	1934–1938 average	1939	1940	Increase, 1940 over 1939, per cent
Intermediates:				
Production	462,614	607,175	805,807	32.7
Sales	197,918	269,084	315,967	17.4
Sales value	28,305	38,489	46,428	20.6
Finished coal-tar products:[b]				
Production	292,873	437,867	522,851	19.4
Sales	251,838	353,604	402,325	13.8
Sales value	106,800	146,156	171,682	17.5
Dyes:				
Production	102,528	120,191	127,834	6.4
Sales	101,137	114,494	122,677	7.1
Sales value	55,227	70,224	76,432	8.8
Medicinals:				
Production	11,596	15,188	18,214	19.9
Sales	9,625	12,932	15,010	16.1
Sales value	9,412	13,711	17,774	29.6
Flavors and perfume materials:				
Production	4,041	5,349	5,485	2.5
Sales	3,757	4,938	5,062	2.5
Sales value	3,354	4,447	4,751	6.8
Resins:				
Production	102,644	179,338	222,943	24.3
Sales	77,891	128,420	153,521	19.5
Sales value	15,271	23,028	33,378	44.9

[a] "Synthetic Organic Chemicals," U.S. Tariff Commission, Washington, 1940.

[b] Includes color lakes, rubber chemicals, and miscellaneous coal-tar products not shown separately.

many and Switzerland. These exports in value and in tonnage exceeded the imports. The present situation regarding the dye production in America is summarized in Table 2, which includes medicinals, flavors, perfumes, and resins, for the reason that these, as well as dyes, are frequently based on the same or analogous intermediates.

The question may well be asked, what do American-made dyes cost? It is quite true that during the shortage years the cost of dyes and intermediates increased greatly in comparison with importations; but as soon as domestic manufacture began to approach consumption, ordinary competition based on improved and cheaper manufacture brought the price down so that now the consumer pays less for his dyes than he did. This is a real and lasting accomplishment.

But, although the dyestuff industry is now an American one and dyes are more economical to the consumer, what about quality? Are American dyes as good as those that were imported from Germany? The answer is an emphatic yes. Most of the dyes made in America are chemical compounds identical to those that were made years ago and are still being made on the banks of the Rhine. Competition in America has in certain instances increased the purity and the strength of the commercially sold dyes. The American dye industry has not been content simply to copy what the rest of the world has done but has pioneered in bringing out new processes for old dyes and intermediates and improved equipment for the cheaper manufacture of both. Indeed many *new* processes for old products have been developed, together with much *new* machinery for carrying out the reactions, and also *new* intermediates and many *new* dyes with numerous improved properties.

This satisfactory state has been accomplished only by continuous research both in the fundamental chemistry involved and in the chemical engineering necessary to commercialize these reactions on an economic

TABLE 3.—RESEARCH COSTS, COAL-TAR PRODUCTS

Year	Net cost of research	Per cent of sales	Technically trained men	Salary per man, average
1928	$2,468,148	3.8		
1929	2,988,769	3.8		
1930	3,432,116	5.2		
1933	3,135,949	4.5	498	$3,548
1934	3,809,546	3.7	664	3,016
1938	5,005,000	3.8	756	2,761
1939	13,064,000[a]	3.5	2,197	3,113
1940	16,200,000[a]	3.3	2,692	2,979

[a] The net cost of research for 1939 and 1940 is not separated into that for aliphatic and coal-tar chemicals but includes all synthetic organic chemicals. This tabulation is compiled from reports of the U.S. Tariff Commission.

scale. Such research has been and is still being carried on. All our large dye factories have well-equipped laboratories and pilot plants either for improving old processes or for developing new. There is no industry other than that making synthetic organic chemicals, that plows back into research such a large proportion of its sales. The actual expenditure for such research is shown in Table 3.

Raw Materials.—The dye industry draws upon every division of the chemical industry for the multiplicity of raw materials needed to make its finished products. However, the backbone of the raw material sequence may be represented in one line:

Coal → coal tar → crudes → intermediates → dyes

Figures 2 and 7 in Chap. VI illustrate the making of the main initial products out of coal and coal tar. The so-called *crudes* are really not crude materials. They *were* 50 years ago, but the skill of the modern chemical engineer has made them, even though sold in large quantities at low prices, almost chemically pure. The name *crude* still persists and applies to the six hydrocarbons obtained by distillation and crystallization from coal tar. We might better call them the *coal-tar dye hydrocarbons.*

COAL-TAR DYE HYDROCARBONS

Benzene
Toluene
Xylene
Naphthalene
Anthracene
Carbazole

In developing the dye industry, America had to manufacture these various hydrocarbons not only of sufficient purity but also in adequate tonnage. This enhanced demand was a tremendous incentive to increasing the installation of by-product coke ovens and the disappearing of the old wasteful beehive ovens. During this period of the development of the dyestuff industry, the production of coke in the by-product oven showed a steady increase from only 27.5 per cent in 1913 to over 96 per cent in 1939. The obtaining of our coke in this manner not only provided basic raw materials for the dye industry but also increased greatly the value of the products derived from coal.

Inorganic Chemicals.—Dyes and intermediates are very heavy consumers of inorganic as well as organic chemicals. The use of these chemicals in the making of dyes and intermediates has frequently been the stimulus for improved processes by virtue of greatly increased demand. This is well exemplified in the development of the contact process for the manufacture of oleum, which came as a further extension of the catalytic oxidation of SO_2 to SO_3, brought about for the need for SO_3 as an oxidizing agent in the old process for converting naphthalene to phthalic anhydride, giving as a by-product sulfur dioxide. Similarly, there is a great demand for chloro-derivatives such as chloro-benzene requiring large tonnages of chlorine. A surprising quantity of inorganic chemicals is frequently required to make 1 lb. of the finished dye, it being estimated that, for some of the indanthrene dyes, up to 75 lb. of such chemicals are required to make 1 lb. of the finished product. Dyes and intermediates consume in general the following chemicals on a large scale:

Acids: Nitric, sulfuric, mixed, hydrochloric, acetic, tartaric, formic, etc.

Alkalies: Caustic soda, soda ash, ammonia, slaked or quicklime (calcium carbonate), caustic potash, and alkylamines.

Salts: Salt (NaCl), sodium sulfate (various forms), sodium nitrite, sodium sulfide, sodium cyanide, copper sulfate, potassium chloride, aluminum chloride, etc.

Miscellaneous: Chlorine, bromine, iodine, hydrogen, alcohol, methanol, formaldehyde, iron, sulfur, etc.

INTERMEDIATES

The intermediates are the building stones out of which dyes are directly constructed, just as our houses are made out of brick, wood, mortar, plaster, or steel, except that chemical reactions are used to connect one intermediate with another in manufacturing a dye. Thus we find the producing of intermediates, economically and in a pure form, to be the very foundation of the dye industry, and the reduction that has come in the last 10 or 15 years in the cost of dyes is due very largely to the lowering of the cost of making pure intermediates. In America this has been achieved through research leading to higher yields in the chemical reactions and to improved chemical engineering when commercializing these reactions. The wise management of our dye factories, stimulated by competition, has directed the study of all the important phases of our factory procedures from which have come lowered labor charges, increased yields, and more uniformity of product, together with enlarged production. This has required the development of improved apparatus in many cases and the courageous discarding of any outmoded plant.

The census of intermediates, taken by the U.S. Tariff Commission, shows that in 1940 there were produced in the United States 665 intermediates,[1] many of them in excess of 500 tons per year, as listed in Table 4. Reference should be made to these annual reports of the Tariff Commission for the very many intermediates made in the United States. A year-to-year comparison will disclose any fundamental change.

These so-called *intermediates* originally were used only to make dyes, but they have now entered into the manufacture of a good many other

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[1] Synthetic Organic Chemicals, U.S. Production and Sales, 1940, *U.S. Tariff Commission Report* 148, 1941.

TABLE 4.—PRODUCTION OF IMPORTANT INTERMEDIATES

Chemical and Trivial Names	Tons Produced, 1940
1-Amino-2-naphthol-4-sulfonic acid (1,2,4 acid)	418
1-Amino-8-naphthol-3,6-disulfonic acid (H acid)	2,155
2-Amino-8-naphthol-6-sulfonic acid (Gamma acid)	651
p-Amino-phenol and hydrochloride	337
Aniline oil	27,859
Benzidine hydrochloride and sulfate	813
Chloro-benzene (sales)	2,400
Chloro-benzoylbenzoic acid	785
o-Cresol	664
o-m-p-Cresols	8,024
Cresylic acid	9,185
o-Dichloro-benzene	2,924
p-Dichloro-benzene	7,543
Dimethyl-aniline	3,524
Dinitro-benzene (D.N.B.)	1,321
Maleic acid and anhydride	2,248
β-Naphthol	Large[a]
2-Naphthol-6,8-disulfonic acid (G acid)	685
1-Naphthylamine-3,6,8-trisulfonic acid	2,370
2-Naphthylamine-1-sulfonic acid (Tobias acid)	939
2-Naphthylamine-5,7-disulfonic acid	738
2-Naphthylamine-6,8-disulfonic acid (Amino-G acid)	991
Nitro-benzene	34,552
Phenol	48,077
Phenylglycine sodium salt	2,097
Phthalic acid and anhydride	28,973
m-Tolylenediamine	540

[a] Probably near to 10,000 tons.

products such as explosives, perfumes, medicinals, flavors, and in particular into resins and plastics. Indeed, the intermediates available from the dye industry have been very largely the starting materials for the building up of our rapidly increasing plastic and resin industries.

Unit Operations, Unit Processes, Energy Changes.—These factors for the intermediate and dye industry are so important that, particularly for the intermediates, a presentation under each main unit process will be made as a logical and technical one. Thereunder will be described[1] the energy changes and any particular unit operation involved in the manufacture, such as special mixing or filtration.

Nitration

Nitration is one of the most important of the unit processes operated for the manufacture of intermediates and dyes. In the industry very few nitro-groups appear in the final product, the nitro-radical being usually reduced to the very reactive amine or subjected to other changes. However, the nitration is frequently the initial side entrance into the aromatic ring whether of benzene or more complicated rings.

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[1] A more detailed presentation, particularly of the chemical and thermal aspects of unit processes as applied to intermediates and many other similar compounds, is given in Groggins, "Unit Processes in Organic Synthesis," 2d ed., McGraw-Hill Book Company, Inc., New York, 1938.

The *agents* used in carrying out nitrations are 40°Bé. nitric acid or mixed acids of varying concentrations, depending upon the reaction and the number of nitro-groups to be introduced. A typical nitration may be expressed as follows:

$$R\cdot H + HNO_3(H_2SO_4) \rightarrow R\cdot NO_2 + H_2O + (H_2SO_4); \quad \Delta H = -15{,}000 \text{ to } -35{,}000 \text{ cal.}$$

To get good yields it is necessary to remove the water formed by the nitration. This is usually done by employing sulfuric acid with the nitric acid (mixed acid) and is frequently expressed as the *dehydrating value of the sulfuric acid* (D.V.S.). Following Groggins (*op. cit.*), the following equation is used:

$$\text{D.V.S.} = \frac{\text{actual 100 per cent sulfuric acid}}{\text{water present in reactants} + \text{water formed by nitration}}$$

Experiments have indicated what D.V.S. is needed for a given nitration but it varies from 2.0 to as high as 12 for technical nitrations. Much *heat* is evolved by the nitration itself as well as by the absorption by the sulfuric acid of the water split out, but the specific heat of the sulfuric acid enables some of this heat to be absorbed. As the higher nitro-compounds may be explosive, a certain amount of precaution is necessary in handling this reaction so as to keep it always under control. Nitric acid is also a powerful oxidizing agent, and this action must be minimized as much as possible by keeping temperatures as low as possible.

The *equipment* used varies from acidproof stoneware, or large nitrators constructed of acidproof brick when using 40° or 42° nitric acid, to cast-iron or stainless-steel nitrators when employing mixed acid; but in every case the unit operations of heat transfer and of mixing should be most carefully considered. The nitration unit process is applied to the making of a number of intermediates among which those in the following list are important.

NITRATION UNIT PROCESS IN MANUFACTURE OF INTERMEDIATES

Chloro-2,4-dinitro-benzene, from chloro-benzene through *o-* and *p*-chloro-nitro-benzene, by strong mixed acid

o- and *p*-Chloro-nitro-benzene, from chloro-benzene by mixed acid. Separate by distillation and crystallization

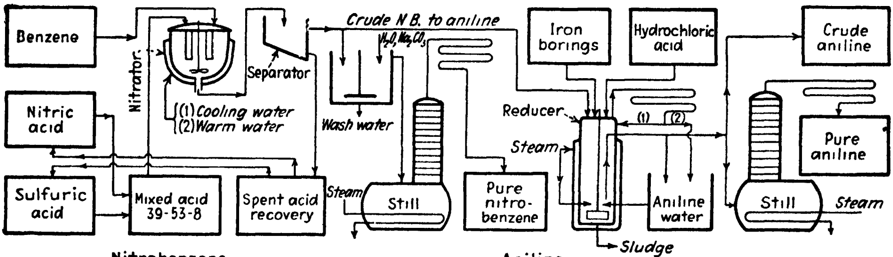
m-Dinitro-benzene, from benzene through nitro-benzene by strong mixed acid

p-Nitro-acetanilide and *p*-nitro-aniline, from acetanilide by cold mixed acid nitration. Hydrolysis furnishes *p*-nitro-aniline
Nitro-benzene, from benzene by mixed acid
Nitro-2,5-dichloro-benzene,[a] from *p*-dichloro-benzene by mixed acid
α-Nitro-naphthalene,[b] from naphthalene by mixed acid
o- and *p*-Nitro-phenol, from phenol by nitric acid or mixed acid. Separate by steam distillation
o- and *p*-Nitro-toluene, from toluene by mixed acid at moderate temperature to lessen oxidation. Separate by distillation and crystallization
m-Nitro-*p*-toluidine, from acyl-*p*-toluidine by mixed acid at low temperature

[a] The nomenclature for these intermediates varies. This compound should be called 2,5-dichloro-nitro-benzene. However, as this book is one in chemical engineering, it should reflect the customary usage of the industry, and this viewpoint leads to the choice of the industrial name.

[b] For further consideration of α-nitro-naphthalene, see Chap. XXXIX.

Example of Technical Nitration.—*Nitro-benzene* is and has been one of the most important intermediates in the dye field, and between 25,000 and 30,000 tons are manufactured yearly. Out of it are made aniline, benzidine, metanilic acid (sulfonation and reduction), as well as dinitro-benzene and certain dyes such as nigrosines and magenta. As the flow sheet in Fig. 1 indicates, nitro-benzene is made by the direct nitration of benzene, using mixed acid, according to the following reaction:



Nitrobenzene

Benzene		1,310 lb
Mixed acid	HNO_3	1,060 lb
	H_2SO_4	1,442 lb
	H_2O	218 lb
Sodium carbonate		20 lb
Power (% total cost)		32
Labor (% total cost)		24
Overhead (% total cost)		83

Per ton Nitrobenzene

Aniline

Nitrobenzene	2,780 lb
Iron borings	3,200 lb
HCl (30%)*	250 lb
Power (% total cost)	64
Labor (% total cost)	80
Overhead (% total cost)	40

Per ton Aniline

* or an equivalent amount of aniline salt mother liquor

FIG. 1.—Flow sheet nitro-benzene and aniline.

$$C_6H_6 + HNO_3(H_2SO_4) \rightarrow C_6H_5NO_2 + H_2O(H_2SO_4); \quad \Delta H = -27{,}000 \text{ cal.}^1$$

This procedure is carried out in cast-iron nitrators arranged with efficient cooling devices to remove the heat of reaction and to keep the procedure under control. In the smaller nitrators a jacket of cooling water will suffice, but for the modern large nitrator taking for instance

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[1] For mononitration of benzene, *cf.* Groggins, *op. cit.*, p. 54.

over 1,000 gal. of benzene, it is necessary to supplement the jacket by other means of cooling.[1]

These additional devices consist of the insertion in the body of the nitrator of water-cooled cast-iron tubes, as indicated in Fig. 1, or the use of steel coils, as in the Hough or Buffalo nitrator. When employing steel coils, because of the greater chance of leakage through a weld, or by reason of corrosion, the water should be sucked through the cooling coils. In case of leakage the acid will enter into the coils and will not do the harm that water would cause if introduced into the nitration mixture under pressure. An electric conductivity automatic indicating device can be easily installed on the exit line of the cooling water to ring an alarm and to light a red lamp whenever any acid is in the exit cooling water. Much of the nitro-benzene is used for further synthesis and can usually be separated from the spent acid and simply given several water washes. If it is to be sold in the pure form, for instance as oil of myrbane as a cheap perfume in the soap industry, it should be distilled.

AMINATION BY REDUCTION

The amino group is an exceedingly important one for dyes as it is the one changed to the azo chromophore or alkylated. This amino radical is also one of the chief auxochromes. It is made by the reduction of a nitro-derivative or recently, in special cases, by ammonolysis (page 849).

The *agents* employed are iron and an acid catalyst, zinc and an alkali, sodium sulfide or polysulfide, with a scattering of less important reagents. The list on page 848 presents some of the aminations particularly pertaining to intermediates. In these and similar lists in this section, a bare indication is given of the process for manufacture. Amines also are made by catalytic hydrogenation and by ammonolysis. More details for those intermediates, not fully treated here, can be found in the books on intermediates in the references at the end of this chapter. The generalized reaction is

$$RNO_2 + 6H \rightarrow RNH_2 + 2H_2O$$

However, for many of our technical aminations by reduction, a better expression would be

$$4RNO_2 + 9Fe + 4H_2O \xrightarrow{\text{Catalyst}} 4RNH_2 + 3Fe_3O_4$$

The *energy* of these reactions is exothermic and so large (see Aniline) that much thought must be given to efficient heat transfer.

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[1] As the size of a given equipment increases, a jacket becomes proportionately less effective, owing to the increase in the contents according to the cube of the corresponding dimension, while the jacket area increases by only the square of the corresponding dimension.

The *equipment* to commercialize these chemical changes is frequently a highly specialized apparatus, as the reducer for aniline. In other cases, particularly when dealing with nonvolatile products like *m*-phenylenediamine, a simple well-ventilated wooden vat performs satisfactorily. However, it should have an efficient sweep stirrer located near the bottom to keep the iron in suspension.

Example of Technical Amination by Reduction. *Aniline.*[1]—This intermediate has been of such great importance that frequently we hear the dyes spoken of as *aniline dyes.*[2] Aniline itself is made by iron reduction of nitro-benzene or by ammonolysis (page 849) of chloro-benzene. A flow sheet exemplifying the iron reduction is included in Fig. 1, and a chart showing production and price changes is in Fig. 2. The reduction can be summarized:

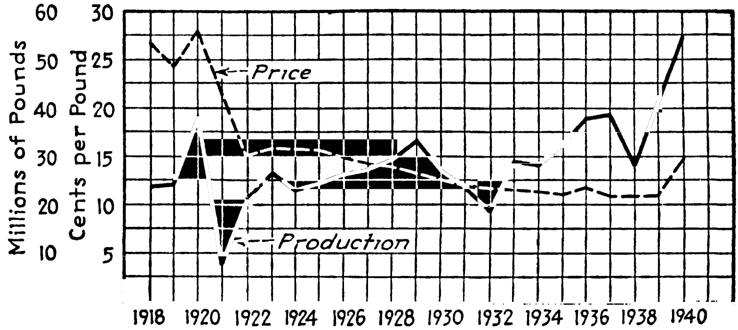
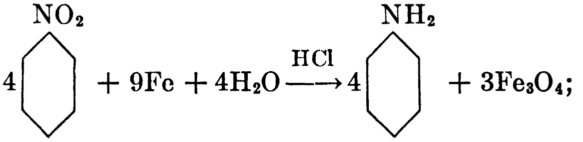


FIG. 2.—Aniline production and price. (*After Weiss.*)



$$4\,C_6H_5NO_2 + 9Fe + 4H_2O \xrightarrow{HCl} 4\,C_6H_5NH_2 + 3Fe_3O_4; \qquad \Delta H = -508{,}000 \text{ cal.}^{3}$$

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[1] For further details in making aniline see Groggins, "Aniline and Its Derivatives," D. Van Nostrand Company, Inc., New York, 1921; Groggins, "Unit Processes in Organic Synthesis," Chaps. 1 and 2; "Rogers' Manual of Industrial Chemistry," 6th ed., sec. VII, Manufacture of Intermediates and Dyes (by Shreve), D. Van Nostrand Company, Inc., New York, 1942.

[2] It is essential from a manufacturing or research viewpoint to know just how many and what dyes are derived from aniline, or any other intermediate. To supply this information the following book was written: Shreve, "Dyes Classified by Intermediates," Reinhold Publishing Corporation, New York, 1922. The book also serves as a dictionary for the various names of the intermediates, as both their chemical and trivial names are arranged alphabetically.

[3] Further consideration of the heat of reaction of aniline manufacture is given in Groggins, "Unit Processes in Organic Synthesis," pp. 76, 97.

In the reduction, as in many other processes, the chemical reactions are much more complicated. These changes can probably be formulated with the sequences listed as follows:

$$
\begin{aligned}
Fe + 2H_2O &\xrightarrow{FeCl_2} Fe(OH)_2 + H_2 \\
C_6H_5NO_2 + 3Fe + 4H_2O &\xrightarrow{FeCl_2} C_6H_5NH_2 + 3Fe(OH)_2 \\
C_6H_5NH_2 + H_2O \longrightarrow C_6H_5NH_3OH &\rightarrow C_6H_5NH_3^+ + OH^- \\
FeCl_2 &\longrightarrow Fe^{++} + 2Cl^- \\
2C_6H_5NH_3^+ + 2OH^- + Fe^{++} + 2Cl^- &\longrightarrow 2C_6H_5NH_3Cl + Fe(OH)_2 \\
C_6H_5NH_3Cl &\longrightarrow C_6H_5NH_3^+ + Cl^- \\
2C_6H_5NH_3^+ + 2Cl^- + 2Fe(OH)_2 + 2Fe &\longrightarrow 2C_6H_5NH_2 + FeCl_2 \\
&\qquad + Fe_3O_4 + 3H_2
\end{aligned}
$$

Note that the iron ends up as the ferroso-ferric oxide. If too little iron is used, the analysis indicates a greater proportion of ferrous iron present, probably as ferrous hydroxide. In actually conducting this reduction on a technical and hence a large scale, it is easy to observe that the chemical change proceeds in stages, for instance, where hydrogen is evolved and when the iron swells owing to hydroxide formation. Such a breakdown into steps is frequently observed when running chemical reactions on a large scale. The iron used for reduction should be cast-iron turnings (or powdered iron) free from oil and nonferrous metals.

Amination by Reduction as Unit Process in Manufacture of Intermediates

Acetyl-*p*-phenylenediamine, from *p*-nitro-acetanilide by iron and acetic acid under 60°C.

α-Amino-anthraquinone, from α-nitro-anthraquinone by Na_2S solution; or by ammonolysis of α-anthraquinone-sulfonic acid

p-Amino-phenol, from nitroso-phenol by aqueous Na_2S; or from *p*-nitro-phenol from *p*-nitro-chloro-benzene

o-Amino-phenol-*p*-sulfonic acid, from *o*-nitro-phenol-*p*-sulfonic acid by Na_2S following sulfonation, nitration, and hydrolysis of chloro-benzene

Aniline, from nitro-benzene by iron and a little dilute HCl

Chloro-toluidine-sulfonic acid, from *o*-chloro-toluene-*p*-sulfonic acid by nitration and subsequent iron reduction

Diamino-stilbene-disulfonic acid, from dinitro-stilbene-disulfonate by alkaline zinc reduction

Diamino-anthraquinone, from corresponding dinitro- or aminonitro-anthraquinone by reduction, or from corresponding dichloro-, disulfo-, or dihydroxy-anthraquinone by ammonolysis

2,5-Dichloro-aniline and sulfonic acid, from nitro-2,5-dichloro-benzene by iron and a little aqueous HCl. Sulfonation

Hydrazoanisole and rearrangement to dianisidine, from *o*-nitro-anisole by alkaline zinc reduction in alcoholic solution, followed by acid rearrangement

Hydrazobenzene and rearrangement to benzidine, from nitro-benzene by alkaline reduction by Fe or Zn, followed by acid rearrangement

Hydrazotoluene and rearrangement to tolidine, from *o*-nitro-toluene by alkaline reduction by Zn followed by acid rearrangement

Metanilic acid, from nitro-benzene-*m*-sulfonic acid, following oleum sulfonation of nitro-benzene
α-Naphthylamine, from *α*-nitro-naphthalene by iron and a little dilute HCl
m-Nitro-aniline, from dinitro-benzene by hot aqueous sodium polysulfide
m-Phenylenediamine, from dinitro-benzene by iron and a little dilute HCl
p-Phenylenediamine, from *p*-nitro-aniline by iron and a little dilute HCl, boiling at the end
Picramic acid, from picric acid by hot sodium polysulfide solution
Toluidines, from nitro-toluenes by iron and a little dilute HCl
m-Tolylenediamine, from *m*-dinitro-toluene by iron and a little dilute HCl
Xylidines, from nitro-xylenes by iron and a little dilute HCl

AMINATION BY AMMONOLYSIS

This unit process has been used for a long time to make *β*-naphthylamine but its extension to aniline and *p*-nitro-aniline is fairly recent. It functions by reacting, usually at elevated temperatures and in autoclaves, with large excess of ammonia water. With the present low cost of ammonia this method of amination has a much more favorable position. The only *agent* used is ammonia or a substituted ammonia which replaces a number of different groups: —Cl, —OH, or —SO_3H.

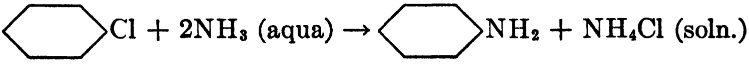
The reaction may be exemplified:

$$R\cdot Cl + 2NH_3 \text{ (aqua)} \rightarrow R\cdot NH_2 + NH_4Cl \text{ (aqua)}$$

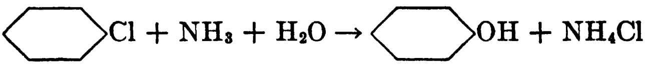
The ammonia is used as aqua-ammonia in large excess, four to ten times theory. Frequently catalysts help speed up the chemical change. As such a large excess of ammonia is necessary for good yields, an efficient recovery system is required to keep costs low. Here then is an excellent example of the unit operation of distillation.

The *equipment* required to commercialize this unit process is almost always some type of agitated pressure vessel made out of ammonia-resisting metal, such as all iron even to the valves. Fortunately the all-iron valves, fittings, pumps, and other equipment previously developed for ammonia ice machines are available at low cost for amination by ammonolysis.[1]

Technical Example. *Aniline.*—The reactions involved in the making of aniline through ammonolysis may be expressed as follows:



(1)



(2)

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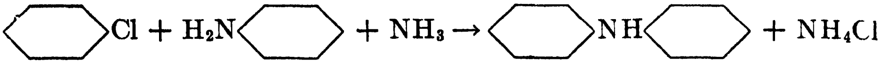
[1] For all these unit processes, reference should be made to Groggins, *op. cit.*, in which are specific chapters covering the details of each unit process.



(3)

$$Cu_2O + 2NH_4Cl \rightarrow Cu_2Cl_2 + 2NH_3 + H_2O \qquad (4)$$

These reactions[1] are carried out using about 4 moles of aqueous 28 to 30 per cent ammonia, first at 180°C. and then for a few hours at 210 to 220°C. under constant agitation. The pressure rises to about 750 lb. Reaction (1) is the desired one, and with the 4 or 5 moles of 28 to 30 per cent NH_3 the formation of phenol [reaction (2)] is to aniline as 1:20. By the use of higher concentrations of ammonia this ratio can be reduced to 1:50, but this larger excess is too costly. The active catalyst is cuprous chloride but by introduction of cuprous oxide (about 1/10 mole) the cuprous chloride is formed and the disadvantageous concentration of NH_4Cl reduced simultaneously. Agitation is secured in a clever manner by the use of horizontal rotating autoclaves.[2] Conversion is about 90 per cent to aniline which can be raised by greatly prolonging the time of reaction, but this is uneconomical.

The products are recovered by blowing off the free ammonia through the recovery and condensing system and separating the oily layer from the aqueous one. The oily layer contains some ammonia, chloro-benzene, aniline, phenol, and diphenylamine, and these are separated by distillation, using normally an alkali, CaO, to hold back the phenol. The aqueous layer is treated with lime to liberate the ammonia and then distilled to recover ammonia and small amounts of chloro-benzene, aniline, and phenol. The copper compound is filtered off and used again. This process gives an excellent grade of aniline.

Amination by Ammonolysis in Manufacture of Intermediates

β-Amino-anthraquinone, from chloro-anthraquinone by excess of 28 per cent aqueous ammonia at 200°C. in a stirred autoclave, or from β-anthraquinone-sulfonate by excess ammonia water

Aniline, from chloro-benzene by excess 28 per cent aqueous ammonia at 200°C. and 900 lb. pressure, in presence of Cu_2O

β-Naphthylamine, from β-naphthol by excess of 28 per cent ammonia aided by ammonium sulfite, at 150°C. in a stirred autoclave

2-Naphthylamine-1-sulfonic acid (Tobias acid) from 2-naphthol-1-sulfonic acid by excess ammonia water and ammonium sulfite at 150°C. in an autoclave

2-Naphthylamine-6-sulfonic acid (Bronner's acid), from sodium salt of 2-naphthol-6-sulfonic acid (Schaeffer's acid) by 28 per cent NH_3 at 180°C. in an autoclave

2-Naphthylamine-6, 8-disulfonic acid (amino-G acid) from 2-naphthol-6, 8-disulfonate by heating with ammonia and sodium bisulfite in an autoclave

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[1] U.S. Patents assigned to the Dow Chemical Company: 1607824 (1926); 1726170, 1726171, 1726172, 1726173, 1729775 (1929); 1775360 (1930); 1823025, 1823026 (1931); 1840760, 1885625 (1932); 1932518 (1933); 2016962 (1935). *Cf.* Groggins, *op. cit.*, pp. 309, 310, 346–349.

[2] These are pictured in *Chem. Industries*, **46**, 690 (1940).

p-Nitro-aniline from p-chloro-nitro-benzene by excess of 28 per cent aqueous ammonia at 170°C. and 500 lb. pressure

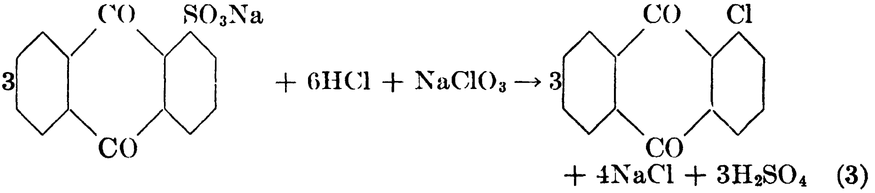
Phthalimide, from molten phthalic anhydride by gaseous NH_3 at 240°C.

HALOGENATION

The use of halogenation and chlorination in particular to effect entrance into a hydrocarbon ring, or other compound, and thus to make a more reactive derivative, is becoming of increasing importance in the field of intermediates as well as in all organic chemistry. The *agent* used is generally dried chlorine gas with or without a catalyst, though other agents like HCl may be necessary for a specific reaction. The chlorination proceeds (1) by *addition* to an unsaturated bond, (2) by *substitution* for hydrogen, or (3) by *replacement* of another group such as —OH or —SO_3H. Examples are

$$CH_2{=}CH_2 + HCl \xrightarrow{\text{Anhydrous}} CH_3CH_2Cl \qquad (1)$$

$$C_6H_6 + Cl_2 \xrightarrow[\text{Anhydrous}]{FeCl_3} C_6H_5Cl + HCl \qquad (2)$$



Reaction (3) proceeds in hot dilute aqueous solution. In certain of halogenation reactions much *heat* is liberated and must be removed (*cf.* chloro-benzene).

The *equipment* necessary is much simplified if anhydrous conditions are called for, as frequently happens. Under these circumstances steel is very satisfactory unless iron and iron compounds exert a disadvantageous effect, when enameled steel or earthenware is used. Nickel is also employed in some special cases.

Technical Example.—*Chloro-benzene* is a very important intermediate particularly for sulfur colors. It is also employed to make many other products such as aniline, phenol, chloro-nitro-benzene and chloro-dinitro-benzene, and *o*-aminophenol-*p*-sulfonic acid. Table 4 indicates sales of over 2,000 tons per year.

Chloro-benzene is manufactured by passing dry chlorine through benzene in iron or lead-lined iron vessels, using ferric chloride as a catalyst. The reaction is as follows:

$$C_6H_6 + Cl_2 \xrightarrow{FeCl_3} C_6H_5Cl + HCl$$

The reaction rate of monochlorination is approximately 8.5 times[1] that of dichlorination, so some dichloro-benzene is always formed. Much heat is generated and, if monochloro-benzene is the preferred product, the temperature should be kept at not over 40 to 60°C., by circulating and cooling the benzene–chloro-benzene mixture. The hydrochloric acid escaping is washed free of chlorine by benzene and absorbed in water for sale. The products of chlorination are distilled to separate the benzene and chloro-benzene, leaving the dichloro-benzenes (ortho and para) in the still residue.

HALOGENATION AS A UNIT PROCESS IN MANUFACTURE OF INTERMEDIATES

Chloro-acetic acid, from glacial acetic acid by passing in chlorine at 100°C. in presence of red phosphorus

Chloro-benzene, from benzene by action of Cl_2 in presence of iron at 50–60°C.

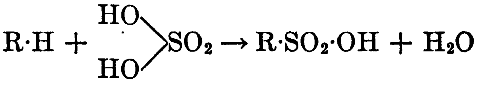
p-Dichloro-benzene, from benzene or chloro-benzene by action of Cl_2 in presence of iron at 50–60°C.

2,6-Dichloro-benzaldehyde, from *o*-nitro-toluene through ring chlorination by Cl_2 furnishing 2-chloro-6-nitro-toluene (40 per cent) and 4-chloro-6-nitro-toluene (60 per cent). These are separated and the 2,6-isomer is subjected to reduction, diazotization, and the Sandmeyer reaction giving 2,6-dichloro-toluene, which upon side-chain chlorination furnishes 2,6-dichloro-benzyl chloride which hydrolyzes to 2,6-dichloro-benzaldehyde

SULFONATION

This is one of the most widely employed of the chemical changes to effect variation in properties such as to introduce greater solubility or to make a hydrocarbon more reactive for the purpose of further synthesis. The fundamental chemistry has been carefully studied[2] and many data are available in the literature. Frequently isomers are formed and the cost of a process will be high unless application can be found for the principal isomers produced. The *agents* employed are various strengths of SO_3 in water from 66°Bé. sulfuric acid or even weaker, to the strongest oleums. However, for special cases, sulfite and chloro-sulfonic acid are very useful. As in nitrations, care should be taken to avoid oxidations by not having temperatures or concentrations too high.

The reaction may be expressed as follows:



$$R{\cdot}H + \begin{matrix}HO\\HO\end{matrix}\!\!>\!SO_2 \rightarrow R{\cdot}SO_2{\cdot}OH + H_2O$$

Depending on what product is being sulfonated there is a critical concentration of sulfuric acid below which sulfonation ceases.[3] Therefore, the removal of the water formed is important. The *energy* of the reaction is exothermic but its removal is often not required, as many sulfonations are carried on at elevated temperatures.

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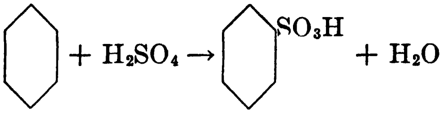
[1] BOURION, *Compt. rend.*, **170**, 1309 (1920).

[2] See volumes by Davidson, Groggins, Reverdin and Fulda, Schwalbe, and Wichelhaus in the references at end of this chapter.

[3] This is summarized by Groggins, *op. cit.*, pp. 266, 277*ff*.

The *equipment*[1] for most sulfonations is fairly simple, consisting of cast-iron vessels provided with an efficient agitator, vent, condenser, and usually a jacket for heating by steam or circulating hot oil. The list on page 855 outlines some of the important industrial sulfonations.

Technical Examples.—*Benzene-sulfonate* is a step in the manufacture of phenol by the sulfonation process. Improvements in this procedure have kept this process competitive with the making of phenol through chloro-benzene. The reaction is as follows:



When the concentration of the sulfuric acid drops below 78 per cent H_2SO_4 (the rest being water), the sulfonating action ceases. At one time, sufficient strong sulfuric acid was used to absorb the water and keep up the concentration. This, however, was a costly procedure, not only wasting sulfuric acid but causing expensive separation of the benzene-sulfonic acid. At present, the water formed is removed by passing benzene vapor through the sulfonation product, thus removing the water by a reverse steam distillation. The ratio of benzene required may be calculated from the formula:[2]

$$\text{Weight of benzene} = \text{weight of water} \times \frac{\text{molecular weight of benzene} \times \text{vapor pressure of benzene}}{\text{molecular weight water} \times \text{vapor pressure of water}}$$

The vapor pressure of the benzene and the water (in presence of sulfuric acid) must be at that temperature at which the sum of the two vapor pressures equals the pressure on the system.[3]

When the water is removed from the sulfonation to keep the acid concentration above 78 per cent H_2SO_4, the sulfonation proceeds until only a few per cent of free sulfuric acid is present which is then directly neutralized to form the sodium salt in conformance with the flow sheet of Fig. 3. The rest of this flow sheet is commented upon under Hydrolysis (page 856).

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[1] SHREVE, Equipment for Nitration and Sulfonation, *Ind. Eng. Chem.*, **24,** 1344 (1932).

[2] Derived from Avogadro's law which states that under the same conditions of temperature and pressure, equal volumes of perfect gases contain the same number of molecules. *Cf.* GROGGINS, "Aniline and Its Derivatives," p. 24.

[3] *Cf.* TYRER, U.S. Pat., 1210725 (1917); GUYOT, *Chimie & industrie*, **2,** 879 (1919); ZAKHAROV, *J. Chem. Ind.*, U.S.S.R., **6,** 1648 (1929).

The 1- and 2-*naphthalene-sulfonic acids* are formed simultaneously by the sulfonation of naphthalene. They must be separated if they are to be used for the preparation of pure naphthols. This is a difficult procedure. However, the alpha acid can be hydrolyzed[1] to the naphthalene and this is distilled out by passing dry steam into the mixed sulfonation mass at around 160°C., leaving behind pure beta acid suitable for hydrolysis or fusion to make β-naphthol.

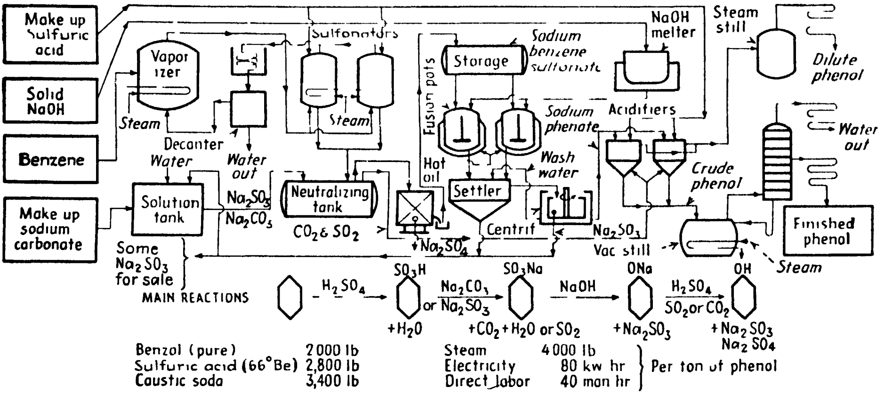

FIG. 3.—Phenol flow sheet—sulfonation process

The usual sulfonation products[2] are more complicated to handle than those just cited, and are illustrated by the examples listed on page 855. The various sulfonic derivatives are frequently difficult to separate from their isomers. The following tabulation gives some of the properties employed for separations or isolations:

1. Variation in the solubilities of the potassium salts.
2. Variation in the solubilities of the calcium or barium or metal salts.
3. Differences in the solubilities of the sulfonic acids themselves in water or acids or other media.
4. Differences in solubilities of the sodium sulfonic salts in presence of a sodium salt such as sodium chloride, sulfate, nitrate, or acetate.
5. Difference in properties of derivatives such as sulfonchlorides or amides.

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[1] SHREVE, β-Naphthol, *Color Trade J.* **14,** 42 (1924). *Cf.* MASTERS, U.S. Pat., 1922813 (1933), and pp. 289, 290, 625–627 of Groggins, "Unit Processes in Organic Synthesis."

[2] For more details regarding sulfonation see the chapter under this heading in Groggins, *op. cit.*, and the books in the references by Fierz-David, Reverdin and Fulda, Wichelhaus. Also see Ullmann, "Enzyklopaedie der technischen Chemie," 2d ed., Urban & Schwarzenberg, Berlin and Vienna, 1928–1932.

SULFONATION UNIT PROCESS IN MANUFACTURE OF INTERMEDIATES

1-Amino-2-naphthol-4-sulfonic acid (1,2,4 acid), from 1-nitroso-2-naphthol by joint reducing and sulfonating action of sodium bisulfite

Benzene-sulfonic acid, by passing hot benzene vapor through sulfuric acid until all sulfuric acid reacted

β-Naphthalene-sulfonic acid, from naphthalene and 66° Bé. sulfuric acid at 160°C.; the α-isomer simultaneously formed is hydrolyzed to naphthalene and removed by passing in steam

Naphthionic acid, from α-naphthylamine sulfate by baking at 170–180°C.

2-Naphthol-6-sulfonic acid (Scheaffer's acid), from β-naphthol by 98 per cent sulfuric acid at 100°C., and separation from the 2:8 acid (Croceine acid) formed simultaneously

2-Naphthol-3,6-disulfonic acid (R acid), from β-naphthol by excess sulfuric acid at low temperatures and separation from G acid

2-Naphthol-6,8-disulfonic acid (G acid), from β-naphthol by excess sulfuric acid at elevated temperature and separation from R acid

1-Naphthylamine-5-sulfonic acid (Laurent's acid) and 1-naphthylamine-8-sulfonic acid from naphthalene by low-temperature sulfonation to the alpha acid, followed by nitration to the two isomers, reduction by iron, and separation

2-Naphthylamine-5,7-disulfonic acid, from β-naphthylamine by oleum sulfonation

2-Naphthylamine-6,8-disulfonic and 2-naphthylamine-5,7-disulfonic acids by sulfonation of β-naphthylamine, first with monohydrate followed by 60 per cent oleum. These acids are separated and fused with NaOH to give, respectively, gamma acid (NOS:286) and J acid (NOS:257)

1-Naphthylamine-3,6,8-trisulfonic acid (Koch acid), from naphthalene by trisulfonation with oleum, followed by nitration and iron reduction

p-Nitro-toluene-*o*-sulfonic acid, from *p*-nitro-toluene by oleum

HYDROLYSIS

In the manufacture of intermediates the phase of hydrolysis employed is usually alkaline fusion to replace an —SO_3H group by —OH. However, this unit process is also operated to replace —Cl, particularly in making phenol. The *agent* generally used is caustic soda, though other alkalies, acids, or plain water are of industrial importance. The reaction may be formulated as follows:

$$\mathrm{ArSO_3Na\ (or\ ArCl) + 2NaOH \rightarrow ArONa + Na_2SO_3 + H_2O} \qquad \mathrm{(or\ NaCl + H_2O)}$$

The *energy* involved is exothermic in many instances. In phenol from chloro-benzene, the heat evolved maintains the reaction temperature.

The *equipment* required is generally either open cast-iron fusion pots heated by gas or closed cast-iron or welded steel autoclaves. Especially in alkaline fusions some loss is experienced from oxidation to tars at the temperatures employed, 300–325°C.

Technical Examples.—*Phenol* is manufactured by the following reactions:

Sulfonation Process:

$$C_6H_5SO_3Na + 2NaOH \xrightarrow{300°C.} C_6H_5ONa + Na_2SO_3 + H_2O$$
$$C_6H_5ONa + CO_2 \text{ (or } SO_2) + H_2O \longrightarrow C_6H_5OH + NaHCO_3 \text{ (or } NaHSO_3)$$

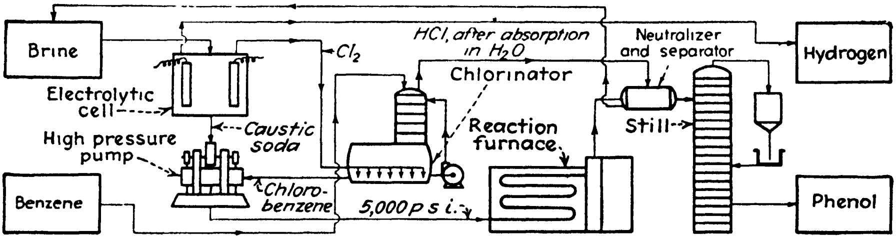
Chloro-benzene Process (Liquid Phase):

$$\begin{aligned} C_6H_5Cl + 2NaOH &\xrightarrow{360°C.} C_6H_5ONa + NaCl + H_2O \\ C_6H_5ONa + HCl &\longrightarrow C_6H_5OH + NaCl \\ C_6H_5ONa + ClC_6H_5 &\longrightarrow C_6H_5OC_6H_5 + NaCl \end{aligned}$$

Catalytic Vapor Phase (or Regenerative Process):

$$\begin{aligned} C_6H_6 + HCl + \tfrac{1}{2}O_2 &\xrightarrow{230°C.} C_6H_5Cl + H_2O \text{ (exothermic)} \\ C_6H_5Cl + HOH &\xrightarrow{425°C.} C_6H_5OH + HCl \text{ (endothermic)} \end{aligned}$$

The older or sulfonation process has held its own competitively, largely because of improvements in procedure such as described under Sulfonation (page 853). Figure 3 outlines the technical steps. It should be noted that either Na_2CO_3 or Na_2SO_3 is used to make the $C_6H_5SO_3Na$, and that either the CO_2 or SO_2 is employed in the acidifiers to liberate or "spring" the phenol. Generally a little diluted H_2SO_4 is necessary to finish the acidification. The fusion is frequently carried out in open cast-iron fusion pots or those with sheet-iron removable covers.



Note Small quantities of copper and sodium oleate are used as catalysts

Caustic Soda 120 lb } To produce 100 lb Phenol
Chlorobenzene 132 lb } and some Diphenyl oxide*

*If no DPO is desired, add 01 mole with reactants

FIG. 4.—Phenol flow sheet—chloro-benzene process.

The chloro-benzene hydrolysis[1] proceeds according to Fig. 4 by pumping a mixture of chloro-benzene and dilute caustic soda through a steel pipe heat exchanger, a reactor, and then through the heat exchanger for cooling. The reactor temperature is about 360°C. and the pressure 5,000 lb. per sq. in. The heat of reaction after the initial start is sufficient to maintain the desired temperature by the use of an efficient heat exchanger. This process affords an excellent application of the unit operations of high pressure, pumping, and heat transfer at high pressure. In order to repress the accumulation of diphenyloxide, about 1/10 mole is added with the reactants.

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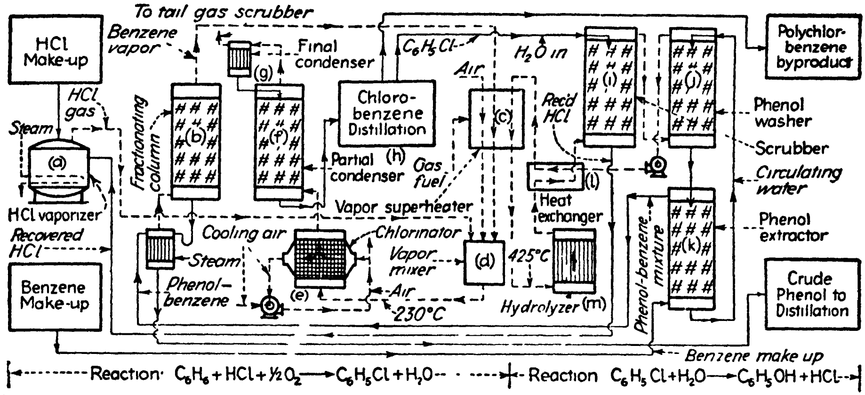
[1] HALE and BRITTON, Development of Synthetic Phenol from Benzene Halides, *Ind. Eng. Chem.*, **20**, 114 (1928); HALE and BRITTON, U.S. Pat., 1607618 (1926); BRITTON, U.S. Pat., 1824867 (1937); GRISWOLD, U.S. Pat., 1833485 (1931); BRITTON, U.S. Pat., 1959283 (1934).



Solid lines represent liquids, dashed lines, vapors and gases. HCl gas from (a) plus benzene vapor from column (b) and air are heated in vapor superheater (c) and mixed in (d), then passed through air-cooled chlorinator (e) (Cu-Fe catalyst). The resulting chlorobenzene mixture is condensed in (f) and (g) (and benzene recovered in the tail gas scrubber), distilled in (h) and the C_6H_5Cl sent, with make-up water, to scrubber (i) where the mixture extracts the phenol from the hydrolysis step and recovers HCl for return to (a). The vapor mixture of C_6H_5Cl, C_6H_5OH and H_2O from (i) passes to washer (j) where the phenol is extracted in water, flowing to extractor (k), and a mixture of C_6H_5Cl and H_2O is vaporized for hydrolysis. The phenol in the water solution is extracted in make-up benzene in (k), the water recirculating to (j) and the benzene-phenol mixture flowing to fractionating column (b) for separation of the crude phenol. The C_6H_5Cl and H_2O vapor from (j) pass through heat exchanger (l), vapor superheater (c), and hydrolyzer (m) (S_1O_2 catalyst) for conversion to C_6H_5OH, the product returning through exchanger (l) to scrubber (i), thus completing the cycle.

FIG. 5.—Phenol flow sheet—vapor-phase regenerative process.

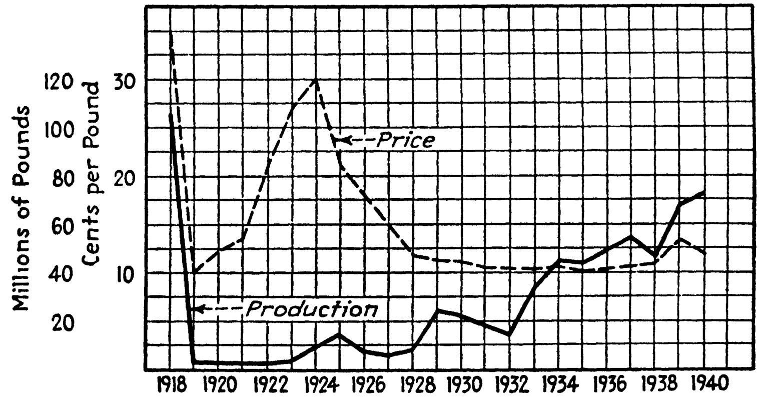


FIG. 6.—Phenol production and price. (*After Weiss.*)

The regenerative or catalytic vapor-phase process is the newest to be installed commercially. It is based on the patents assigned to Raschig.[1] This procedure has been recently described and pictured in the literature.[2] It presents some very interesting engineering problems, particularly as to the handling of hot HCl in the presence of steam and air. The conversions are low and require much recirculation. Figure 5 shows the sequences of unit operations and unit processes that represent the commercialization of the basic chemical changes.

Phenol is used for a great variety of products: dyes, plastics, explosives, medicines, and perfumes. Its economic position is shown by the production and selling price curves of Fig. 6.

β-Naphthol is made somewhat similarly to the phenol sulfonation process. The conditions for the hydrolysis (alkali fusion) of the 2-naphthalenesulfonate are given in the references under Sulfonation.

HYDROLYSIS (OR IN MANY INSTANCES "ALKALI FUSION") IN MANUFACTURE OF INTERMEDIATES

1-Amino-8-naphthol-3,6-disulfonic acid (H acid), from 1-naphthylamine-3,6,8-trisulfonic acid by caustic-soda fusion in an autoclave
2-Amino-5-naphthol-7-sulfonic acid (J acid), from 2-naphthylamine-5,7-disulfonic acid by caustic-soda fusion in an autoclave
2-Amino-8-naphthol-6-sulfonic acid (gamma acid), from 2-naphthylamine-6,8-disulfonic acid by caustic-soda fusion in an autoclave
1,5-Dihydroxyanthraquinone (anthrarufin), from anthraquinone-1,5-disulfonic acid by milk of lime
1,8-Dihydroxynaphthalene-3,6-disulfonic acid (chromotropic acid), from 1-naphthol-3,6,8-trisulfonic acid by caustic-soda fusion at 200°C.
2,4-Dinitro-phenol, from chloro-2,4-dinitro-benzene by boiling with soda-ash solution
β-Naphthol, from purified β-naphthalenesulfonate (naphthalene and hot sulfuric acid) by caustic-soda fusion
α-Naphthol, from purified α-naphthalenesulfonate (naphthalene and cold sulfuric acid) by caustic-soda fusion, or from α-naphthylamine
1-Naphthol-4-sulfonic acid (Nevile-Winther's acid) from sodium naphthionate by heating with NH_4HSO_3 (Bucherer reaction)
p-Nitro-aniline, from *p*-nitro-acetanilide, by boiling with caustic-soda solution
o- or *p*-Nitro-phenol, from *o*- or *p*-chloro-nitro-benzene by hot dilute $NaOH$ solution
Phenol from benzene-sulfonate by caustic-soda fusion at 320°C.
Phenol from chloro-benzene by caustic-soda solution at 360°C., 5,000 lb. pressure
Phenol from chloro-benzene by H_2O at 425°C.

OXIDATION

Oxidation is controlled or tempered combustion and is one of the very useful unit processes for the entire organic technology. The cheapest *agent* is air, but oxygen is sometimes employed. For liquid-phase reactions a great many oxidizing agents are in industrial use, such as permanganates, dichromates, chromic anhydrides, hypochlorites, chlorates, lead peroxide, and hydrogen peroxide. Water and carbon dioxide and many other oxidized substances are the by-products of the main oxidation.

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[1] RASCHIG, U.S. Pat., 1963761, 2009023, and 2035917 (1935).

[2] ANON., New Synthetic Phenol Plant, *Ind. Eng. Chem., News Ed.*, **18**, 921 (1940); OLIVE, *Chem. & Met. Eng.*, **47**, 770 (1940); **47**, 789 pictured flow sheet; **46**, 222 (1939); GROGGINS, *op. cit.*, pp. 630–633, detailed description.

When charcoal or carbon (amorphous) changes to carbon dioxide, $\Delta H = -96{,}500$ cal.[1] per g.-mole and when hydrogen burns to H_2O (gaseous), $\Delta H = -57{,}800$ cal. per g.-mole. These *energy changes*, although the basis of combustion, frequently accompany our controlled oxidation, as in the making of phthalic anhydride (page 860) and maleic acid. In most oxidations, even when the formation of CO_2 and H_2O can be repressed, the energy change is exothermic and large. This entails particular care in the design and construction of the *equipment* so as to ensure efficient heat transfer and to prevent the controlled oxidation from becoming a combustion.

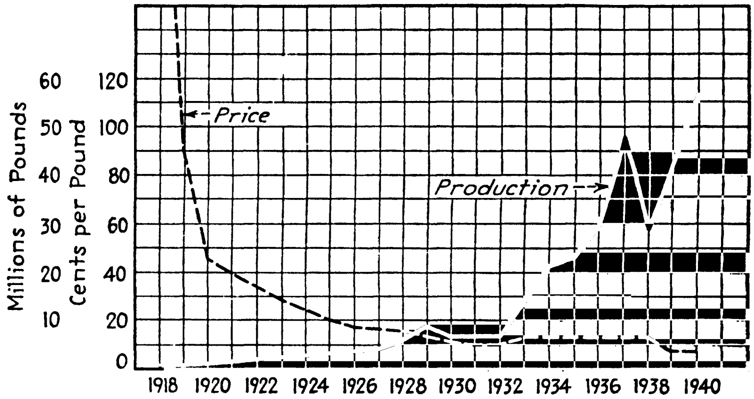


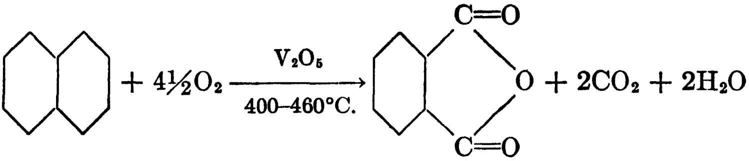
Fig. 7.—Phthalic anhydride production and price. (*After Weiss.*)

Technical Example.—*Phthalic anhydride* has become one of our most important intermediates. It is used in making directly a number of dyes such as eosin, erythrosin, and phenolphthalein, but it is of more value as a step in manufacturing anthraquinone and anthraquinone derivatives by Friedel-Crafts procedure (page 864), where it has opened up the entire anthraquinone vat dyes to the American market at reasonable prices. Figure 7 presents the production and price trends. These products are consumed also in industries other than dyes, as in making resins and plasticizers. Phthalic anhydride and phenol are two among many intermediates whose consumption has expanded far beyond dyes.

---

[1] For carbon, the equivalent in B.t.u. per pound 14,400; for hydrogen 52,000 B.t.u. from 1 lb.

The present process for phthalic anhydride[1] is a controlled catalytic air oxidation of naphthalene.



$\Delta H = -5{,}460$ B.t.u. per lb. naphthalene oxidized. If the naphthalene is burned completely to CO_2 and H_2O, 18,000 B.t.u. per lb. of naphthalene are liberated. Actually, when manufacturing phthalic anhydride by this process, an exothermic reaction of from 6,000 to more than 10,000 B.t.u. per lb. of naphthalene is observed, owing to a certain amount of complete combustion that always occurs.

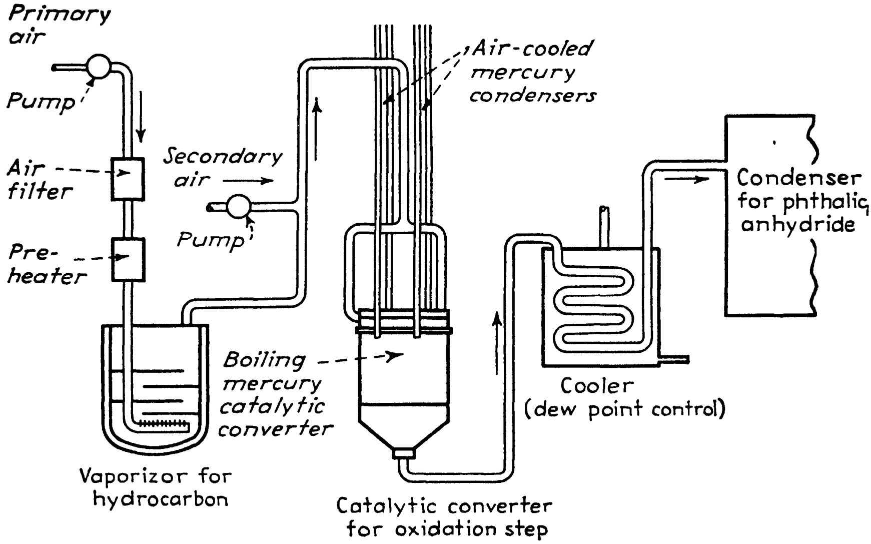

Primary air
Pump
Air filter
Pre-heater
Secondary air
Pump
Air-cooled mercury condensers
Condenser for phthalic anhydride
Boiling mercury catalytic converter
Cooler (dew point control)
Vaporizor for hydrocarbon
Catalytic converter for oxidation step

FIG. 8.—General layout for phthalic anhydride process using Downs' reactor.

This process, with a suitable catalyst, was discovered by Gibbs and Conover.[2] It was also necessary to work out efficient equipment to remove the great amount of heat liberated and to keep the temperature within the favorable narrow limits. One of the successful devices is that patented by Downs[3] and depicted in principle in Figs. 8 and 9. It consists of square tubes (to increase surface in relation to volume) carrying the V_2O_5 catalyst, surrounded by mercury. This mercury by its boiling removes the heat of reaction, and the hot mercury vapor preheats the entering naphthalene vapor and then passes on to the condenser. In the Downs reactor the temperature is nicely controlled by raising or lowering the boiling point of mercury by the raising and lowering of the pressure of an inert gas (nitrogen) on the mercury boiling and condensing system.

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[1] DOWNS, Oxidation of Aromatic Hydrocarbons, *Ind. Eng. Chem.*, **32**, 1294 (1940), bibliography; CONOVER, Economics of Catalytic Oxidation in the Vapor Phase, *Ind. Eng. Chem.*, **32**, 1298 (1940).

[2] U.S. Pat., 1285217 (1918).

[3] U.S. Pat.; 1604739 (1926). Also DOWNS, U.S. Pats., 1374020, 1373021 (1921); 1789809 (1931); and 1873876 (1932).

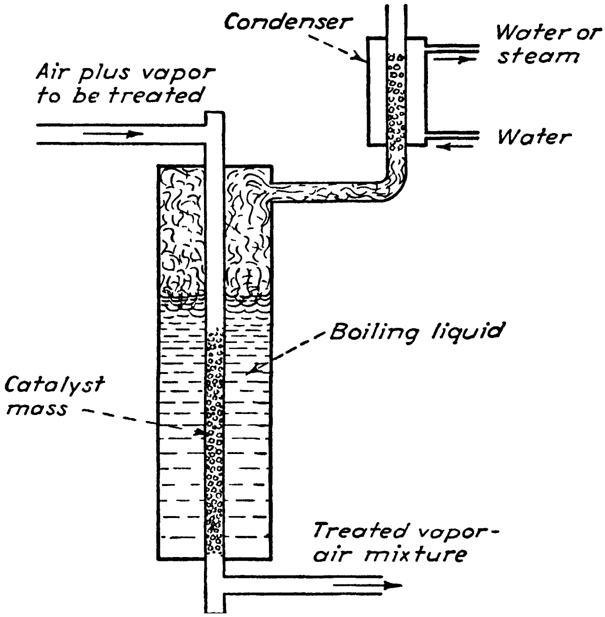

FIG. 9.—Apparatus for removal of reaction heat by boiling of a liquid. (*After Marek and Hahn.*)

Other heat-transfer media have been proposed, such as sulfur, diphenyl, diphenyl oxide, mercury amalgams, and mixed nitrate-nitrite.[1] The products from the reaction are rapidly cooled to about 125°C. (approximately the dew point of phthalic anhydride) and are then sublimed[2] into large chambers or towers in which the phthalic anhydride condenses in needle crystals.

OXIDATION UNIT PROCESS IN MANUFACTURE OF INTERMEDIATES

Anthranilic acid, from phthalimide by alkaline hypochlorite
Anthraquinone, from anthracene by chromic acid
1,4-Dihydroxy-anthraquinone (quinizarin), from anthraquinone by sulfuric acid oxidation in presence of boric acid
Dinitro-stilbene-disulfonic acid, from *p*-nitro-toluene by sulfonation and alkaline NaOCl oxidation
Phthalic anhydride, from naphthalene by air oxidation at 425°C. in presence of vanadium pentoxide

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[1] KIRST, NAGLE, and CASTNER, *Trans. Am. Inst. Chem. Engrs.*, **36**, 37 (1940).

ALKYLATION

Although alkylation of a hydroxyl is used occasionally in the dye field to reduce solubility of phenol derivatives, its most extensive application is in alkylating amines, as will appear from inspection of the list on page 863. The *agents*[1] employed are exceedingly varied but an alcohol such as methanol, or an alkyl halide, or a dialkyl sulfate is frequently employed

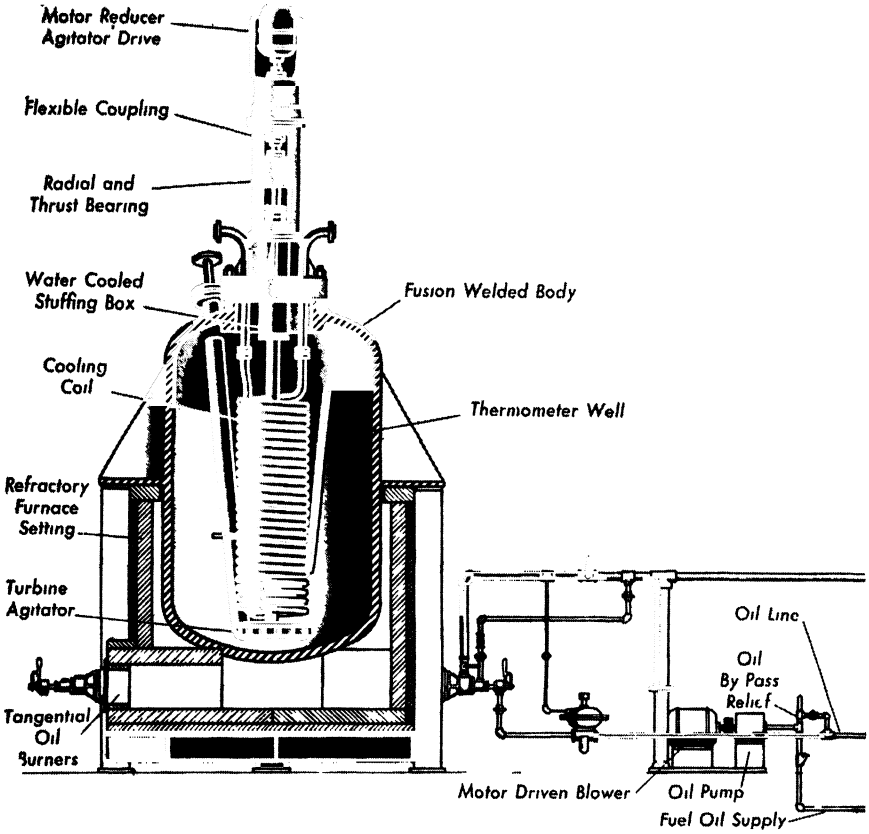

FIG 10 —A complete autoclave installation engineered by Blaw-Knox

The *equipment* used quite often requires pressure to keep the reactants in the desired liquid state. Such an autoclave is depicted in Fig. 10. For autoclaves of small size, jackets are frequently convenient for heating; in the larger sizes an interior coil, such as shown in this figure, enables more heating surface to be available than would be possible from a jacket.

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[1] See GROGGINS, *op cit*, pp 485*ff*, on Alkylation by Shreve

Furthermore, it is advantageous to have the corrosion concentrated on the more easily replaceable coil than on the more expensive shell.

Technical Example.—*Dimethyl-aniline* is employed extensively in the manufacture of a number of triarylmethane dyes. It is prepared according to the following reaction:

$$C_6H_5NH_2 + 2CH_3OH \xrightarrow{H_2SO_4} C_6H_5N(CH_3)_2 + 2H_2O$$

Aniline, with a considerable excess of methanol and a little sulfuric acid, is heated in an autoclave, such as shown in Fig. 10, at around 200°C. for 5 or 6 hr., the pressure rising to 525 or 550 lb. The product can be tested by noting any rise in temperature when mixed with acetic anhydride, to ascertain if any monomethylaniline is still present. If monomethyl is low or absent, the alkylation product can be discharged under its own pressure through a cooling coil, neutralized, and vacuum-distilled.

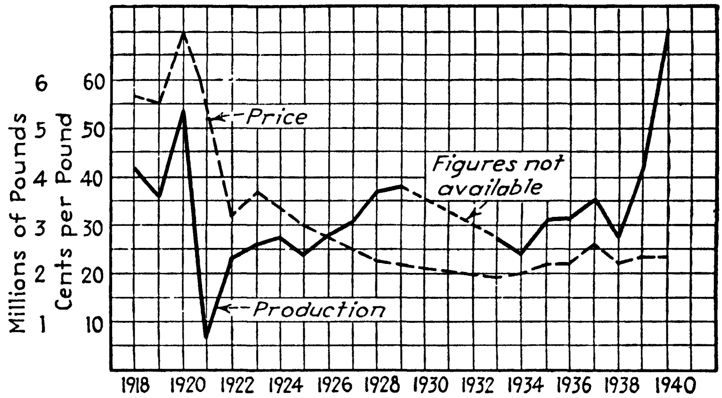


FIG. 11.—Dimethyl-aniline production and price. (*After Weiss.*)

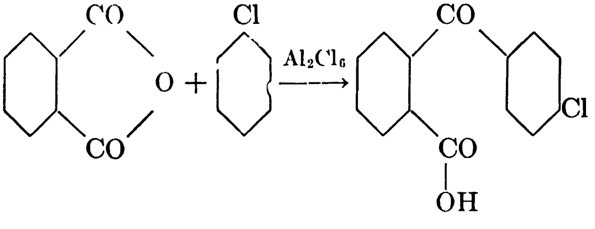
ALKYLATION UNIT PROCESS IN MANUFACTURE OF INTERMEDIATES

Benzyl-ethyl-aniline (and sulfonic acid), from ethyl-aniline and benzyl chloride
Diethyl-aniline, from aniline, ethyl alcohol, and a little HCl in an autoclave, or from aniline and diethyl sulfate
Dimethyl-aniline, from aniline, methanol, and a little sulfuric acid at 200°C. in an autoclave
o-Nitro-anisole, from *o*-chloro-nitro-benzene by methanol and caustic soda

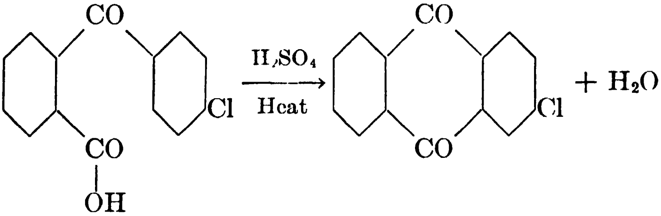
FRIEDEL-CRAFTS REACTION

The list on page 864 gives only four products that are manufactured in any considerable tonnage, but this unit process is used in the making of a great many different chemicals. The three intermediates listed in the table are, however, the basis of some of our most useful vat dyes. The *agent* employed in this reaction is usually an acid anhydride or an acid chloride, always catalyzed by aluminum chloride. A typical example of this unit process involves the making of *p*-chloro-benzoylbenzoic acid according to the following reactions:

Friedel-Crafts to Furnish p-Chloro-benzoylbenzoic Acid:



Condensation or Ring Closure to Furnish β-Chloro-anthraquinone:



Typical *equipment* necessary to carry out this Friedel-Crafts reaction and that of the following ring closure is sketched in Fig. 16 wherein are also listed the approximate conditions and proportions. The industrial significance of the Friedel-Crafts reaction coupled with the ring closure to make anthraquinone or anthraquinone derivatives as the basis for the fast vat dyes for cotton cannot be overestimated. Without these processes the manufacture of vat dyes would be much more costly, as the American tar distillers do not produce cheap anthracene.

FRIEDEL-CRAFTS UNIT PROCESS IN MANUFACTURE OF INTERMEDIATES

Benzanthrone, from naphthalene, benzoyl chloride, and $AlCl_3$ to α-benzoylnaphthalene to benzanthrone (benzanthrone is also condensed from anthranol and glycerine by aid of sulfuric acid)

Benzoylbenzoic acid, from phthalic anhydride, benzene, and aluminum chloride

p-Chloro-benzoylbenzoic acid, from phthalic anhydride, chloro-benzene, and aluminum chloride

p-Methyl-benzoylbenzoic acid (for 2-methyl-anthraquinone), from phthalic anhydride, toluene, and aluminum chloride

MISCELLANEOUS UNIT PROCESSES

The following list presents, in outline, a selection of the most important intermediates that have not been included in the unit processes considered in this section. Details on their manufacture can be readily obtained from the references under Intermediates at the end of this chapter.

VARIOUS MISCELLANEOUS UNIT PROCESSES IN MANUFACTURE OF INTERMEDIATES

Condensation:
- β-Hydroxy-naphthoic acid anilide, from β-hydroxy-naphthoic acid and aniline
- Phenyl-glycine, from aniline and chloro-acetic acid
- Phenyl-1-naphthylamine-8-sulfonic acid, from 1-naphthylamine-8-sulfonic acid, aniline, and aniline hydrochloride by heating in an autoclave
- Tetramethyldiamino-benzophenone (Michler's ketone), from dimethyl-aniline (2 moles) and phosgene
- Tetramethyldiamino-diphenylmethane, from dimethyl-aniline, (2 moles) and formaldehyde in presence of hydrochloric acid

Acylation:
- Acetanilide, from aniline by heating with glacial acetic acid
- Acetyl-*p*-toluidine, from *p*-toluidine by heating with glacial acetic acid

Carboxylation:
- β-Hydroxy-naphthoic acid, from sodium β-naphtholate and CO_2 under pressure at 200°C.
- Salicylic acid, from dry sodium phenate and CO_2 under pressure and at 140°C.

Miscellaneous:
- Aminoazo-toluene (and sulfonate), from *o*-toluidine to diazoamino-toluene, and molecular rearrangement
- Anthraquinone (ring closure), from *o*-benzoylbenzoic acid by sulfuric acid
- Benzoic acid, from phthalic acid by decarboxylation
- 2-Chloro-anthraquinone (ring closure), from *p*-chloro-benzoylbenzoic acid by sulfuric acid

DYES

Many of us have a feeling of bewilderment when we view the complicated chemical formula representing a typical dye. However, if we recall the analogy between our houses and our dyes and view the dyes, as well as the houses, as being built out of simpler materials put together in an orderly fashion, these complicated structures become much simplified. As the architect changes the period or style of a house by varying the use of the same fundamental materials, wood, brick, stone, and steel, so the chemist makes different dyes by varying the chemical reactions to which he subjects the same intermediates. The dyes are built up out of more than 500 intermediates by a dozen or so important unit processes that unite one or more of these intermediates into a new chemical individual which, if it has the right structure, becomes a dye.

Figures 12 to 14 present a tabular outline of the sequences in the procedures from the basic coal-tar hydrocarbons through the intermediates to a number of characteristic dyes, all by subjecting first the hydrocarbons and then the intermediates to the chemical changes (unit processes when commercially applied). This chapter includes a number of typical intermediates and dyes, and in their presentation the chemical changes necessary for their fabrication are given.[1] Attention is called to the names of the dyes in Figs. 12 to 14 as being both chemical and the most used commercial designations. The dyes are classified both chemically (by structure) and by application (by use).

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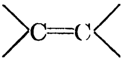
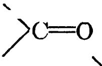
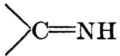
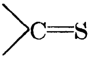
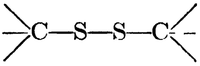
[1] From the selected references at the end of this chapter further details can be obtained, particularly for the intermediates from the volumes by Groggins, David-

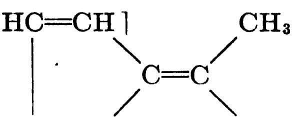
Cause of Color.—*A certain amount of unsaturation in the dye molecule with part of it at least in the form of aromatic rings combined with the quinoid structure of a minimum complexity usually lays the foundation of the molecules that we recognize as dyes.* Much has been correlated between chemical structure and color,[1] and the earlier conceptions promulgated by the dye chemists in this field are still helpful. We may write the equation

$$\text{Dye} = \text{chromogen} + \text{auxochrome}$$

The *chromogen* is an aromatic body containing a group called a *chromophore.* By derivation, chromophore means *color-giver* and is represented by such chemical radicals as the following:

1. The nitroso group: $—NO$ (or $=N—OH$)
2. The nitro group: $—NO_2$ (or $=NO{\cdot}OH$)
3. The azo group: $—N{=}N—$
4. The ethylene group: 
5. The carbonyl group: 
6. The carbon-nitrogen groups:  and $—CH{=}N—$
7. The sulfur groups:  and 

Such groups add color to the simpler aromatic bodies by causing displacement of, or an appearance of, absorbent bands in the visible spectrum. These chromophores are so important that we chemically classify many of our dyes by the chief chromophore that they contain. These chromophore groups are capable of reduction and, if this is carried out, the color frequently disappears, probably owing to the removal of electron resonance. Close packing of unsaturation, as conjugation, also tends toward color. Thus even the hydrocarbon dimethylfulvene:



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son, or Cain, and for the dyes from the books by Rowe, Schultz, and Georgievics. NOTE: When this book is used as a college text, an excellent assignment would be to have the students fill in the necessary chemical changes in Figs. 12 to 14.

[1] WATSON, "Colour and Its Relation to Chemical Constitution," Longmans, Green and Company, New York, 1918. A very excellent correlation of the various theories of color is in the introduction to Georgievics and Grandmougin, "A Textbook of Dye Chemistry," Scott, Greenwood and Son, London, 1920.

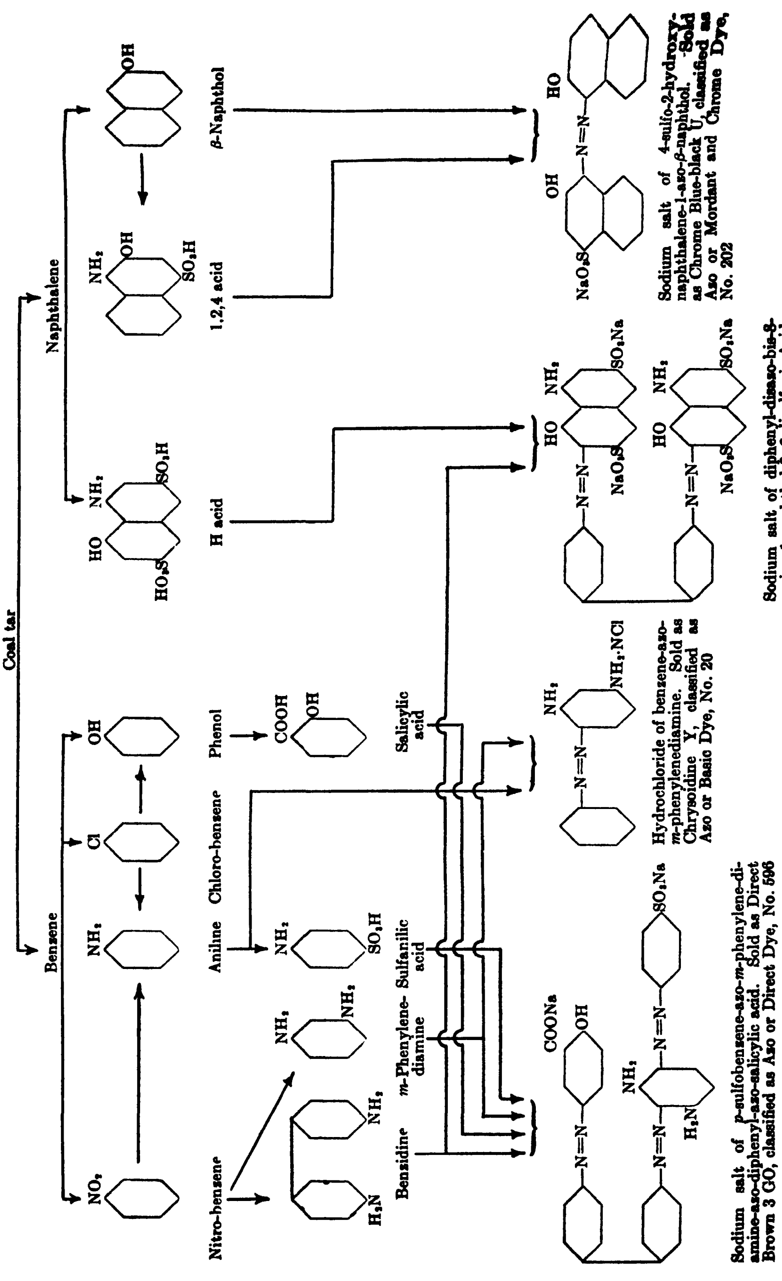

Coal tar
Benzene
Naphthalene
NO_2
NH_2
Cl
OH
Nitro-benzene
Aniline
Chloro-benzene
Phenol
COOH
OH
Salicylic acid
HO
NH_2
HO_3S
SO_3H
H acid
NH_2
OH
SO_3H
1,2,4 acid
OH
β-Naphthol
H_2N
NH_2
NH_2
NH_2
NH_2
SO_3H
Benzidine
m-Phenylene-diamine
Sulfanilic acid
COONa
OH
N=N
NH_2
H_2N
N=N
SO_3Na
Sodium salt of p-sulfobenzene-azo-m-phenylene-diamine-azo-diphenyl-azo-salicylic acid. Sold as Direct Brown 3 GO, classified as Azo or Direct Dye, No. 596
N=N
NH_2
$NH_2 \cdot HCl$
Hydrochloride of benzene-azo-m-phenylenediamine. Sold as Chrysoidine Y, classified as Azo or Basic Dye, No. 20
N=N
HO
NH_2
NaO_3S
SO_3Na
N=N
HO
NH_2
NaO_3S
SO_3Na
Sodium salt of diphenyl-disazo-bis-8-amino-1-naphthol-3, 6-disulfonic Acid. Sold as Direct Blue 2 B, classified as Azo or Direct Dye, No. 406
NaO_3S
OH
N=N
HO
Sodium salt of 4-sulfo-2-hydroxy-naphthalene-1-azo-β-naphthol. Sold as Chrome Blue-black U, classified as Azo or Mordant and Chrome Dye, No. 202

FIG. 12.—Relationship of coal tar, hydrocarbons, intermediates, and some azo dyes.

has an orange color. Although it may be colored, a chromogen may lack the chemical affinities necessary to make the color adhere to the textile fiber. Thus assistant groups, or *auxochromes*, are needed, which are usually salt-forming groups such as —NH_2, —OH, their derivatives, or the solubilizing radicals —COOH or —SO_3H. These auxochromes, chromophores, and chromogens will be very apparent by following the

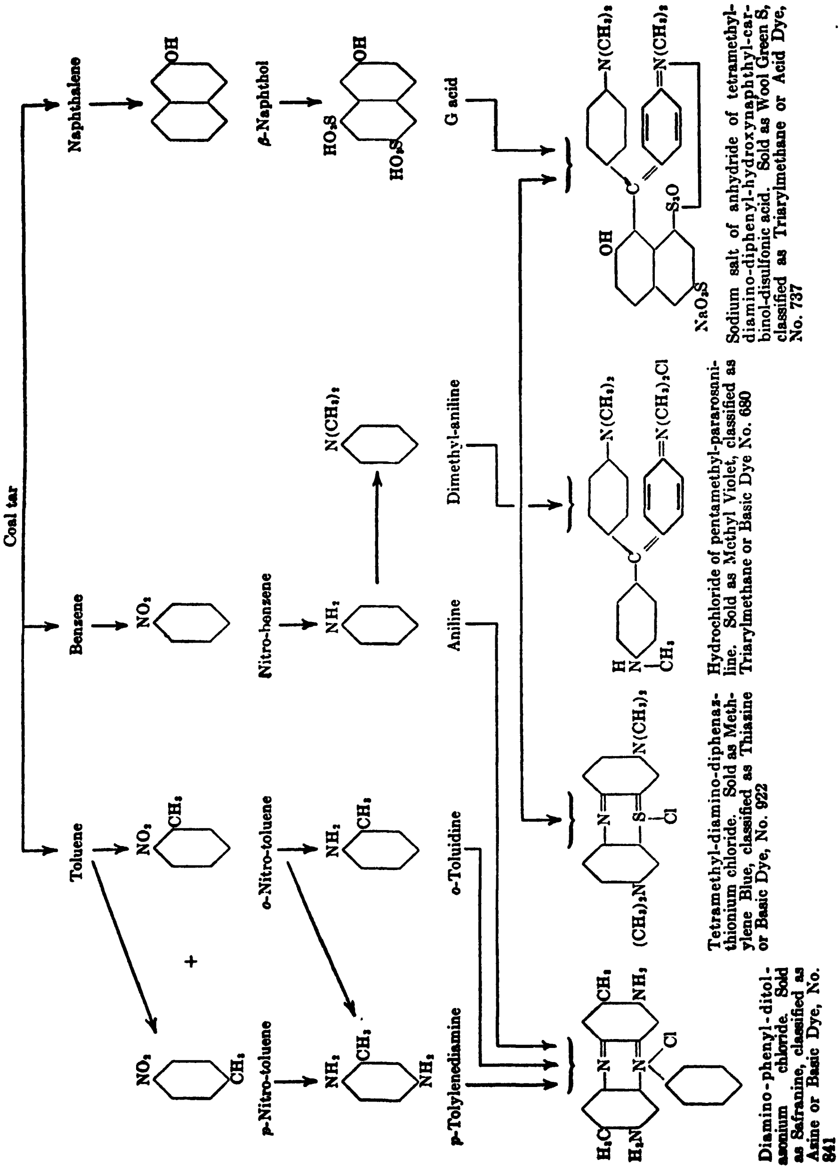

Coal tar
Naphthalene
β-Naphthol
G acid
Benzene
Nitro-benzene
Aniline
Dimethyl-aniline
Toluene
o-Nitro-toluene
o-Toluidine
p-Nitro-toluene
p-Tolylenediamine
Sodium salt of anhydride of tetramethyl-diamino-diphenyl-hydroxynaphthyl-carbinol-disulfonic acid. Sold as Wool Green S, classified as Triarylmethane or Acid Dye, No. 737
Hydrochloride of pentamethyl-pararosaniline. Sold as Methyl Violet, classified as Triarylmethane or Basic Dye No. 680
Tetramethyl-diamino-diphenazthionium chloride. Sold as Methylene Blue, classified as Thiazine or Basic Dye, No. 922
Diamino-phenyl-ditolazonium chloride. Sold as Safranine, classified as Azine or Basic Dye, No. 841

FIG. 13.—Relationship of coal tar, hydrocarbons, and some azine thiazine, and triarylmethane dyes.

classification of dyes, but the assisting radicals such as —OH, —NH$_2$, —SO$_3$H, and —COOH have usually more influence on placing a dye in a given use group directed toward dyeing a certain fiber, rather than in a chemical structural classification.

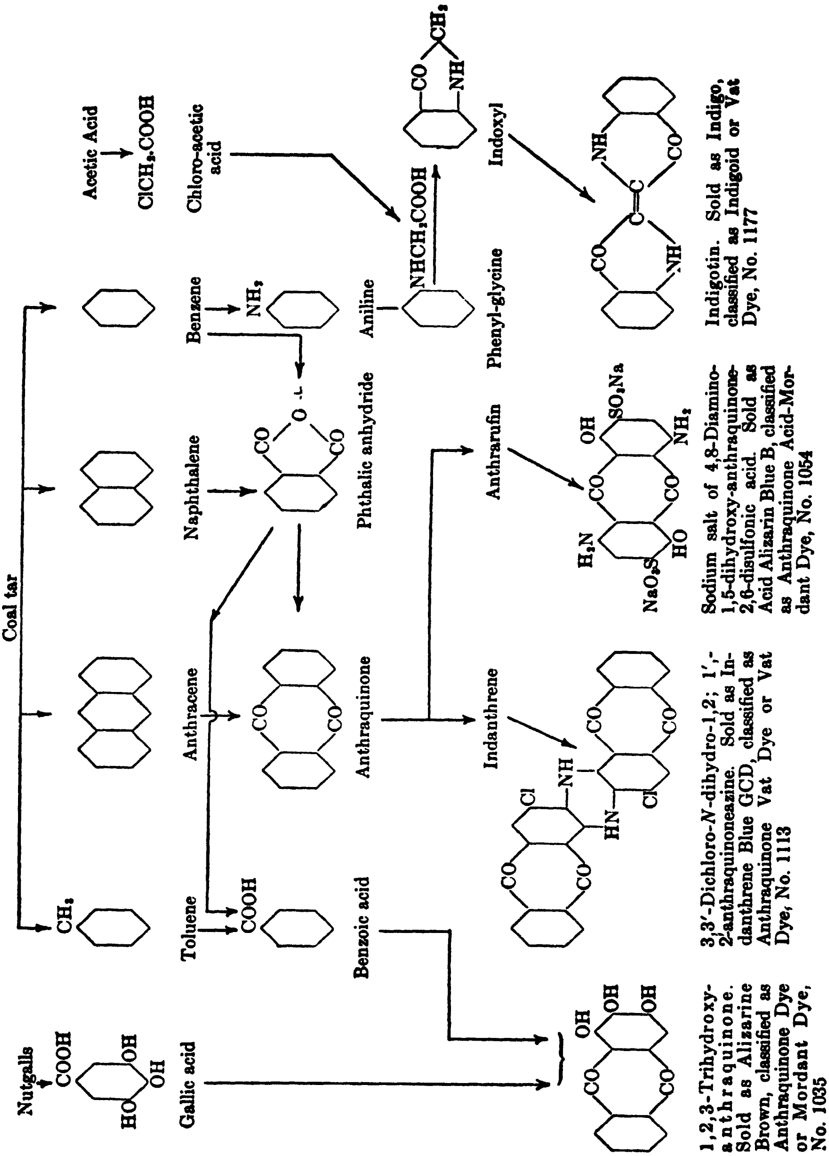
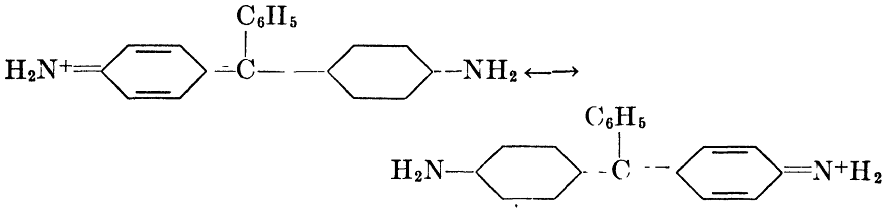

Coal tar
Nutgalls
COOH
OH
OH
HO
Gallic acid
CH$_3$
Toluene
COOH
Benzoic acid
Anthracene
CO
CO
Anthraquinone
Naphthalene
CO
O
CO
Phthalic anhydride
Benzene
NH$_2$
Aniline
NHCH$_2$COOH
Phenyl-glycine
Acetic Acid
ClCH$_2$.COOH
Chloro-acetic acid
CO
CH$_2$
NH
Indoxyl
Anthrarufin
Indanthrene
OH
OH
OH
CO
CO
1,2,3-Trihydroxy-anthraquinone. Sold as Alizarine Brown, classified as Anthraquinone Dye or Mordant Dye, No. 1035
CO
CO
Cl
Cl
NH
HN
CO
CO
3,3'-Dichloro-N-dihydro-1,2; 1',2'-anthraquinoneazine. Sold as Indanthrene Blue GCD, classified as Anthraquinone Vat Dye or Vat Dye, No. 1113
H$_2$N
NaO$_3$S
HO
CO
CO
OH
SO$_3$Na
NH$_2$
Sodium salt of 4,8-Diamino-1,5-dihydroxy-anthraquinone-2,6-disulfonic acid. Sold as Acid Alizarin Blue B, classified as Anthraquinone Acid-Mordant Dye, No. 1054
CO
NH
C=C
NH
CO
Indigotin. Sold as Indigo, classified as Indigoid or Vat Dye, No. 1177

FIG. 14.—Relationship of coal tar, hydrocarbons, intermediates, and indigo with some anthraquinone dyes.

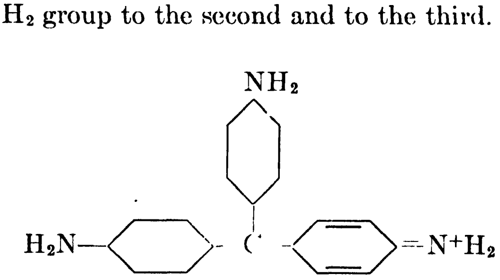
None of these color theories fully satisfies all the facts, but the above have been exceedingly useful in working out new dyes and giving some understanding of the entire color picture. Probably resonating chemical structures are of great importance in explaining why chromophores, auxochromes, and unsaturation cause color.

Resonance[1] has been proposed as a general explanation of the cause of color, and this subject has been studied further by Lewis and Calvin.[2] As Burg writes, "the intense absorption of light that characterizes dyes is due to an intimate association of a chromophore and of resonance in a molecule." The auxochromes, besides influencing the attachment of dyes to the fiber, increase the possibility of resonance. Assuming with Lewis and Calvin that in the absorption of light that causes color, the energy is taken up by electronic oscillations, and as resonance is the oscillation or movement of electronic pairs without the shifting of atoms, then the resonance theory of color presupposes the absorption of light by the oscillating electrons in these resonating structures. Both Burg with Lewis and Calvin submit much interesting evidence to show that resonance, as well as other electronic disturbances, and color are closely related. Several examples must suffice here: Döbner's Violet is assumed to exist in the two resonating forms:



wherein the resonating electrons absorb the light. This is a simple but not a commercial dye; however, in Magenta (C.I. 677)[3] we would have opportunity for three resonating structures, as the pair of electrons would move from one $—NH_2$ group to the second and to the third.

Magenta



[1] Burg, Auxochromes and Resonance, *J. Am. Chem. Soc.*, **57**, 2115 (1935).

[2] Lewis and Calvin, Color of Organic Substances, *Chem. Rev.*, **25**, 273–278 (1939).

[3] C.I. 677 refers to Rowe, "Colour Index and Supplement," Society of Dyers & Colourists, Bradford, Yorkshire, 1924 and 1928; here dyes are numbered serially.

Testing of Dyes.—In the use of dyes it is of the utmost importance to know such properties as fastness, solubility, and method of dyeing.[1] There are various types of fastness for dyes, all relative to one another. It is essential to know, in properly evaluating and applying a dye, its fastness not only to light but also to perspiration, acids, and alkalies, rubbing, sea water, and carbonizing. American-made dyes are as fast as any others in the world, being the same chemical compounds here as abroad.

Classification of Dyes.—Dyes are classified from both the chemical and the application viewpoints. The manufacturers look at dyes from the *chemical* aspect and arrange and manufacture them in groups usually of like unit processes; this frequently brings similar chromophores together. Thus, dyes that contain the azo chromophore are found manufactured in a building that may be called the *azo building.* On the other hand, a similarity in grouping of those that contain the indigoid radical is found. This very largely parallels the modern unit process way of classifying and looking at applied organic reactions. Not only do the factories arrange dyes in this way but the books presenting the properties of dyes so classify them, among which we may particularly cite the volumes by Schultz and by Rowe.[2]

In this chapter the various dyes are presented under this chemical classification. On the other hand, the users of dyes group them according to the methods of *application.* A dyer engaged in coloring silk is particularly interested in the type of dye that gives good results on this fiber and not specially in dyes that color cotton only. We do not always have this sharp differentiation in application; indeed, we have certain dyes that are union dyes and will color more than one fiber. There are three broad divisions that we wish to color: those products of vegetable origin, those from animals, and those made artificially. Cotton, linen, and paper are of a vegetable nature and essentially consist of cellulose. On the other hand, the products of animal origin that we wish to dye are much more reactive and consist of such substances as silk, wool, feathers, fur, and leather. The artificial fibers consist principally of viscose rayon which dyes quite similarly to cotton, it being also essentially cellulose, and acetate rayon which is an ester and requires special dyes. The following are the main types of dyes in our *application* classification:

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[1] The books herein referred to, particularly those by Rowe ("Colour Index and Supplement,") and by Knecht, Rawson, and Lowenthal give such properties. However, the yearbooks of the American Association of Textile Chemists and Colorists present each year the latest methods for testing fastness of dyes together with recent references to the literature.

[2] See Selected References at the end of this chapter.

Acetate rayon
Acid
Azoic
Basic
Direct cotton
Lake or pigment
Mordant or chrome
Sulfur or sulfide
Spirit-soluble
Vat
Food
Photographic
Medicinal
Bacteriological
Indicator

The U.S. Tariff Commission presents dyes by both the use and the chemical classification. Table 5 gives the production of the different dyes by their use.

TABLE 5.—COMPARISON OF UNITED STATES PRODUCTION OF DYES, BY CLASSES OF APPLICATION, AVERAGE 1934–1938, ANNUALLY 1939 AND 1940[a]

Class of application	Production					
	Quantity, 1,000 lb			Per cent of total		
	1934–1938 average	1939	1940	1934–1938 average	1939	1940
Acetate silk	1,961	2,585	2,548	1.9	2.2	2.0
Acid	13,849	17,700	17,179	13.5	14.7	13.5
Azoic	1,077	3,318	3,629	1.1	2.8	2.8
Basic	5,149	6,415	6,926	5.0	5.3	5.4
Direct	25,780	31,433	32,863	25.1	26.2	25.8
Lake and spirit-soluble	2,765	3,305	3,883	2.7	2.7	3.0
Mordant and chrome	5,262	5,237	6,957	5.1	4.4	5.4
Sulfur	16,619	18,651	21,561	16.2	15.5	16.9
Vat, total	29,234	30,035	30,076			
Indigo	15,378	12,475	11,133	15.0	10.4	8.7
Other	13,856	17,560	18,943	13.5	14.6	14.8
Unclassified	831	1,506	2,212	0.9	1.2	1.7
Total	102,527	120,190	127,834	100.0	100.0	100.0

[a] "Synthetic Organic Chemicals," U.S. Tariff Commission, Washington, 1940.

The *acetate*[1] *rayon* dyes are those which have been specially developed to dye cellulose acetate and similar fibers. They may be broadly divided into two general groups embracing insoluble simple azo dyes and insoluble anthraquinone[1] colors, both in a highly dispersed type and consequently capable of penetrating or dyeing the acetate fiber. Aminoazo compounds have been solubilized by the use of an omega sulfonic acid group that splits off during the dyeing. These are sold as the ionamines[2] in England, but these water-soluble acetate dyes have not attained any considerable sale in the United States. Early examples of the dispersed dyes are the S.R A. wherein the dispersing agent is sulfo-ricinoleic acid (hence the designation S.R.A.). Until these and similar special dyes for acetate were developed, the selling of acetate rayon was much handicapped.

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[1] For acetate dyes, see Thorpe, "Dictionary of Applied Chemistry," 4th ed., Longmans, Green and Company, New York, 1937; Vol. 1, 1939. For an excellent generalized presentation of dyeing, *cf. ibid.*, Vol. 4, pp. 120–188; "Rogers' Manual of Industrial Chemistry," 6th ed., D. Van Nostrand Company, Inc., New York, 1942. However, the standard text in the field of dyeing or dye application is Knecht, Rawson, and Lowenthal, "Manual of Dyeing," 8th ed., 2 vols., Charles Griffin & Company, Ltd., London, 1925. See Rose, The Mechanism of Dyeing, *Am. Dyestuff Reptr.*, **31**, 204–211 (1942). For a very good summary of dyeing embracing the principal application classes as well as a consideration of the kinetics of dyeing, see Lewis, Squires, and Broughton, "Industrial Chemistry of Colloidal and Amorphous Materials," pp. 505–518, The Macmillan Company, New York, 1942.

The *acid* dyes are used to color animal fibers from acidified solutions, probably by combining with the amphoteric proteins of such fibers. The acid auxochromic or solubilizing groups, $—NO_2$, $—SO_3H$, and —COOH frequently aided by —OH, are usually present in the acid dye, whether the fundamental chemical structure be that of the azo, triarylmethane, or anthraquinone complex. These acid dyes are employed in about 75 per cent of all wool dyeing and are also of importance in silk dyeing. Such dyes are somewhat deficient in fastness to alkalies and soap, though usually possessed of good color resistance. Examples are Orange II, 151, and Acid Black 10B, 246, among the azos, and Acid Alizarine Blue B, 1054, among the anthraquinone dyes.

The *azoic* dyes embrace those insoluble azos which are made on or in the fiber. Here the actual coupling reaction is made to take place after one or both of the constituents have been allowed to penetrate the fiber. These were called *developed* or *ice* or *ingrain colors*. As a rule, those direct colors which are further built or *developed* on the fiber by the diazotization and coupling reactions are not classified under the azoic use division. The azoic dyes are increasing in application very markedly, owing to better methods of building up the dye on the fiber by the use of stabilized diazotized amines. If, for example, an azo dye is so insoluble that it cannot be made to enter the fabric, it nevertheless will give excellent fastness resistance in many instances if made in the fiber out of soluble reactants. These dyes are almost always applied only to cotton. Typical reactions leading to their formation are given under the azo chemical classification.

Basic dyes are mostly amino, or substituted amino, derivatives frequently from the triarylmethane or xanthene class but they are applied mostly to cotton and linen and, with the aid of the tannin mordants, they dye animal substances directly such as wool, silk, leather, feathers, and fur from a neutral bath. They are also employed in printing designs on cotton for calicoes and shirtings. An interesting application of the basic dyes is in typewriter ribbons and carbon papers where Methyl Violet, 680, and Crystal Violet, 681, are widely employed. Other examples are Bismarck Brown, 332, and Chrysoidine, 20, for leather dyeing, together with Auramine, 655, and Malachite Green, 657, for textiles. The basic dyes are of unusual brilliancy and of high tinctorial power, but their fastness to light is often unsatisfactory.

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[1] Rowe and Chamberlain, Dyeings on Cellulose Acetate Rayon, *J. Soc. Dyers Colourists*, **53**, 268 (1937); Kartaschoff and Farine, The Dyeing Phenomena of Acetate Artificial Silk, *Helv. Chim. Acta*, **11**, 813 (1928).

[2] Green and Saunders, U.S. Pat., 1483084 (1924); Duisberg and Hentrich, U.S. Pat., 1757419 (1930).

The *direct* dyes are frequently from the azo class and are used to dye cotton or the vegetable fibers. Some of them are also employed for dyeing union goods (cotton and wool, or cotton and silk). As this dyeing is usually aided by the addition of common salt, or Glauber's salt, to the dye bath, such dyes have been called *salt dyes*. The salt decreases the solubility of the dye and hence causes better exhaustion of it from the dyeing solution. They are also called *substantive* colors. Examples are Direct Blue 2B, 406, Direct Black EW, 581, Direct Brown 3GO, 596, and many others. A number of direct dyes possessed of free NH_2 groups can be *developed* on the fiber thus increasing their insolubility and hence their fastness to washing. This developing is by the processes of *diazotizing* the free amino group and then *coupling* with the developer which may be β-naphthol (*cf.* azo dyes, page 884).

Lake or *pigment* dyes form insoluble compounds or lakes with salts of Ca, Ba, Cr, Al, or phosphomolybdic acid. The dye molecule frequently contains —OH or $-SO_3H$ groups. Such lakes, when ground in oil or other media, form the pigments of many of our paints and inks. In this use class fall such dyes as Lithol Red R, 189, Ponceau 2R, 79, Orange II, 151, and the splendid new phthalocyanines (pigments).

The *mordant* or *chrome* dyes are applied principally to wool wherein by the use of a mordant which may be chromium or less frequently aluminum or iron, the fastness to light and washing is much increased. Such dyes contain —OH or $-COOH$ radicals frequently attached to azo or anthracene (anthraquinone) complexes. The mordant dyeing is really a metallic salt or lake formed in the fiber. Examples are Alizarin, 1027, Chrome Blue Black U, 202, Gallocyanine, 883, and many others.

The *sulfur* or *sulfide* dyes contain a chromophore with sulfur and are also dyed from a sodium sulfide bath, wherein the sulfur color is reduced to a colorless or light-colored leuco derivative. Schiemann[1] represents the change as follows:

$$\equiv C—S—C\equiv \longleftrightarrow \equiv C—SH + HC\equiv$$

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[1] SCHIEMANN, "Die Chemie der naturlichen und künstlichen organischer Farbstoffe," p. 96, Leopold Voss, Leipzig, 1936.

Sulfur dyes are usually applied on cotton and form a large, low-priced, and useful group, among which we find Sulfur Black, 978, as the most extensively sold single dye (basis dry weight). These dyes furnish dull shades of excellent fastness to light, washing, and acids.

The *vat* dyes, including the long-used indigo, are those whose chemical structure is such that reduction furnishes an alkali soluble and usually colorless "vat" with which the fiber, generally of vegetable origin such as cotton, is impregnated. This, upon exposure to air, oxidizes back to the insoluble color. Such dyes are of complicated chemical structure such as indanthrenes but furnish dyes of exceptional fastness to light, alkaline washing, perspiration, and even chlorine. The vat dyes furnish the fast-dyed cotton shirtings and dress goods and, although expensive, are rapidly increasing in use. The vat dyes are likewise made in a paste with alkaline hydrosulfite-aldehyde reducing agent, printed on the cloth and passed through an oxidizing bath of sodium bichromate or perborate. Examples are Indigo, 1177, Indanthrene Blue GCD, 1113, and Anthraquinone Vat Yellow GC, 1095.

The *spirit-soluble* or oil-soluble dyes are frequently simple azos or triarylmethane bases used to color oils, waxes, varnishes, shoe dressings, lipsticks, and gasoline. *Food* dyes are of various structure, selected and tested for harmlessness and employed in coloring foods, candies, and confections. The *photographic*, *medicinal*, *bacteriological*, and *indicator* dyes are highly specialized products of relatively small sales volume but of fundamental importance in the maintenance of our national economy.

MANUFACTURE OF DYES

The very distinguished and pioneering English chemist, Sir William Henry Perkin, is the father of the synthetic organic chemical dyes.[1] Not only did he discover[2] the first practical synthetic aniline dye, *Mauve*, which is made of toluidine, containing aniline, by oxidation, but he organized with his father and brother a company to make synthetic dyes, designed and built the equipment to manufacture Mauve and other dyes, and went out into the dyeing establishments to show how to apply his products. In the early years, from 1856 on, Perkin *was* the dye industry. After 17 years of success, he sold out to enjoy a life of research and investigation. In the meanwhile the Germans took up the dye industry and rapidly became the leaders in the field until 1914, when the Americans,

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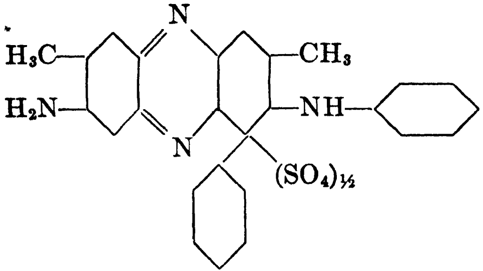
[1] An authoritative, logical, and readable presentation of this industry is in the booklet by Rowe, "Two Lectures on the Development of the Chemistry of Commercial Synthetic Dyes (1856–1938)," Institute of Chemistry, London, 1939.

[2] Perkin's first patent for a synthetic dye was taken out Aug. 26, 1856, English Pat., 1984 of 1856. Initially his yields on Mauve, or as he early called it, *Aniline Purple*, were only 5 per cent.

English, and other nations intensively cultivated this line of manufacture as an essential industry.



Mauve, 846

Industrially there are used now in the United States over 1,000 different dyes of which 500 are made in appreciable tonnage,[1] some, such as Sulfur Black, Indigo, Direct Black EW, and Developed Black BHN, amounting in production to more than 1,000 tons annually for each one.

To present some of the outstanding dyes we shall arrange them by the chemical (or chromophore) classification, such as nitro, nitroso, azo dyes, but include also the application designation. Dyes have entered the markets of the world with a *variety of names for the same chemical individual.* Such are listed in the indexes and tabulations of a number of books.[2] The usual name adopted here is that appearing in the annual reports of the U.S. Tariff Commission to which is added the C.I. number definitely to distinguish a specific chemical compound among the many names under which it may be marketed.

The commercial names are frequently followed by letters, some of which have special designations, among which may be listed:

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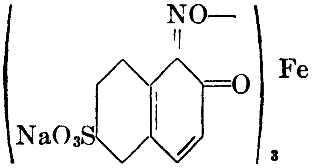
[1] "Synthetic Organic Chemicals, U.S. Production and Sales," U.S. Tariff Commission, Government Printing Office, Washington, yearly. This report of production and sales of dyes, intermediates, and other organic chemicals should be in the hands of everyone interested in this field, as it supplies most up-to-date statistics on the entire organic field. Not only are current tonnages available, but trends are seen by comparison of different years.

[2] ROWE, *op. cit.;* SCHULTZ, "Farbstofftabellen," 7th ed., Akademische Verlagsgesellschaft m.b.H., Leipzig, 1931. These two volumes have the commercial dyes numbered and arranged under the chemical classification with references to patents and other literature, together with data on properties both chemical and dyeing, and with directions for making. SHREVE, "Dyes Classified by Intermediates," Reinhold Publishing Corporation, New York, 1922, also lists the multitudinous names under which dyes are sold. The yearbook of the American Association of Textile Chemists and Colorists, Howes Publishing Co., New York, presents such names particularly for the American manufacturer. The list is very extensive, embracing over 150 pages.

B	bluish, BB or 2B, more bluish.
G	yellowish (*gelblich*), occasionally greenish.
R	reddish.
S	bisulfite compound or sulfonic derivative or dye for silk.
W	for wool, HW for part wool, WS for wool and silk.
L	easily soluble (*löslich*), lake forming, or for linen.

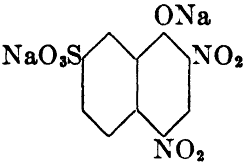
From a manufacturing aspect, dyes fall naturally into their chemical classification, which also is identical with that in the tabulations by Rowe and Schultz (page 876). The presentation will follow this long-accepted arrangement.

Nitroso or Quinone Oxime Dyes.—Chromophore: —NO (or =N—OH). Only two members of this class are listed as produced in America by the U.S. Tariff Commission: *Fast Printing Green*, C.I. 2, and *Naphthol Green B*, C.I. 5. The latter is an acid dye, is used in wool and pigment dyeing, and is made by the action of nitrous acid on 2-naphthol-6-sulfonic acid and conversion to the ferric sodium salt.



Nitro Dyes.—Chromophore: —NO_2 (or =NO·OH). The only nitro dye that is reported as made in the United States is *Naphthol Yellow S*, C.I. 10, which is a cheap acid dye for clear yellow shades on wool and silk, now little used because of low light stability. It is a dye permitted in foods. Its chemical name is sodium 2,4-dinitro-1-naphthol-7-sulfonate, and it is manufactured by sulfonating α-naphthol to 1-naphthol-2,7-disulfonic acid or 1-naphthol-2,4,7-trisulfonic acid, and then nitrating, thus replacing one or two sulfonic groups.

Naphthol Yellow S, 10



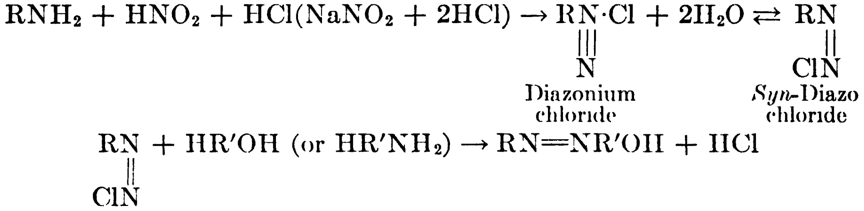
Azo Dyes.—Chromophore:[1] —N=N—. This class exemplifies the application of the unit process of diazotization and coupling. Over half of the dyes of commerce fall within this classification, of various degrees of complexity according to the number of azo groups contained or of the assisting or auxochrome groups. Pursuing the chemical classification, we

[1] Reynolds, Color and Constitution of Azo Dyes, *Am. Dyestuff Reptr.*, **32**, 455 (1943)

name subgroups under the azo dyes as monoazo, disazo, trisazo, or tetrakisazo dyes, depending upon whether there is present one, two, three, or four azo groups. And, as we may vary the chemical skeleton and the number and nature of the auxochrome groups, we obtain basic or mordant, acid or direct dyes, or indeed members of all the use classes except vat and sulfur dyes. After the fundamental principles of the reactions were worked out, following the basic discovery by Peter Griess[1] in 1858, literally thousands of azo dyes were made and their properties investigated. Those which survived are the azo dyes that possess suitable properties of fastness or ease of dyeing.

Azo dyes can be made soluble or insoluble as the central rings, or the auxochromes, are changed. They *can* be made actually on or in the fiber,[2] or another azo group can be added to an azo dye already on the fiber (developed colors), or a stabilized diazo derivative can be coupled with a suitable intermediate, both being on the fiber (stabilized azoics). This flexibility of formation leads to useful dyes of a great variety of properties.

The fundamental reactions may be expressed as follows:



$$RNH_2 + HNO_2 + HCl(NaNO_2 + 2HCl) \rightarrow \underset{\substack{\text{Diazonium}\\ \text{chloride}}}{\underset{\displaystyle N}{\underset{|||}{RN{\cdot}Cl}}} + 2H_2O \rightleftarrows \underset{\substack{Syn\text{-Diazo}\\ \text{chloride}}}{\underset{\displaystyle ClN}{\underset{\|}{RN}}}$$

$$\underset{\displaystyle ClN}{\underset{\|}{RN}} + HR'OH \text{ (or } HR'NH_2) \rightarrow RN{=}NR'OH + HCl$$

These two reactions are known as *diazotization* and *coupling*. Specifically, the energy change in diazotizing in aqueous solution and thus forming diazobenzene hydrochloride may be expressed:[3]

$$C_6H_5{\cdot}NH_2{\cdot}HCl + HNO_2 \rightarrow 2H_2O + C_5H_5N_2Cl; \qquad \Delta H = -22{,}800 \text{ cal.}$$

For α-naphthylamine subjected to the same reaction, $\Delta H = -24{,}820$ cal.

Fortunately for their wide industrial application these reactions can usually be carried out almost quantitatively,[4] if the temperature is kept low; this is done by the use of ice.

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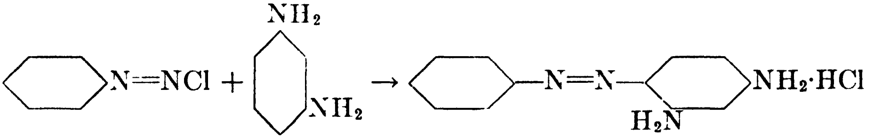
[1] GRIESS, *Ann.*, **106**, 123 (1858).

[2] Ice or ingrain or developed colors, now called *azoics*.

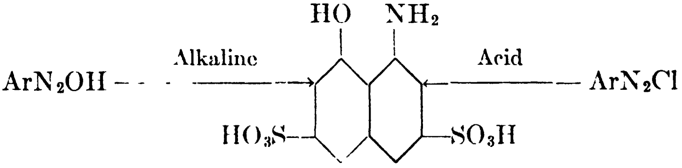
[3] CAIN, "Chemistry and Technology of the Diazo Compounds," p. 32, Edward Arnold & Co., London, 1920. *Cf.* SAUNDERS, "Aromatic Diazo Compounds and Their Technical Applications," pp. 78–79, Longmans, Green and Company, New York, 1936.

[4] There are a number of books that present these reactions in various aspects. Particularly pertinent is the chapter on Diazotization and Coupling by Woodward in Groggins "Unit Processes in Organic Synthesis." *Cf.* O'BRIEN, "Factory Practice in the Manufacture of Azo Dyes," Chemical Publishing Company, Inc., New York, 1924. See also references at the end of this chapter.

There are specific rules for the coupling of an amine or of a phenol to a diazo body.[1] Generally the diazo solution is to be run into the arylamine, phenol, naphthol, or derivative, though there are some exceptions, as *Chrome Blue Black U* exemplified in Fig. 15. With phenols and naphthols the coupling is usually *para* to the hydroxyl group or, if this position is occupied, then the *ortho* place is taken. However, the very important β-naphthol couples only once and in the *one* position. Amines couple less readily than do phenols; the coupling takes place only in the *para* position. Of the diamines the *meta* derivatives react most easily, the coupling taking place *para* to one —NH₂ group and *ortho* to the other. This is frequently called the *Chrysoidine law* and is exemplified in the making of *Chrysoidine G*, C.I. 20.



Substituents and pH influence coupling. For instance, H acid,



has the position *ortho* to the —NH₂ group activated in acid solutions, and the coupling takes place there, while the activation in alkaline solutions is *ortho* to the —OH with coupling in this position; thus H acid can couple twice. The important amino-naphthol-sulfonic acids, gamma acid and J acid, can couple only once but the position is influenced also by the pH. This property is of very great technical importance in governing the formation of azo derivatives of proper shade and of desired fastness.

Table 6 lists important azo dyes under the azo subclasses and the application class. This table also gives the intermediates from which the dye is derived.[2] Following the rules of coupling just enumerated, the structure of these dyes can be determined.

The equipment in which azo dyes are manufactured by diazotization and coupling is quite simple in comparison to that used for most other unit processes. It is exemplified in Fig. 15 depicting the making of *Chrome Blue Black U*, C.I. 202, and consists largely of wooden stirred tanks of various sizes, wooden plate-and-frame filter presses, drying boxes wherein on steel carts the dye, previously placed on trays, is dried by circulating hot air. Sometimes sensitive dyes are dried in vacuum shelf driers. The milling, mixing, and standardizing of dyes end the manufacturing sequence. The mills must be so chosen as not to ignite the sensitive dyes. Frequently ball mills provided even with wooden balls are indicated. As customers require absolute uniformity in dyes, the mixing and standardizing are of utmost importance. The double-cone dye mixer and blender, sometimes used, has no internal parts to hold up a dye and performs the mixing and blending in an unusually satisfactory manner.[1]

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[1] SAUNDERS, *op. cit.*, Chap. VI, pp. 102–124; pp. 73*ff.*

[2] *Cf.* SHREVE, "Dyes Classified by Intermediates," *op. cit.*, for extensive tables of dyes under each constituent intermediate.

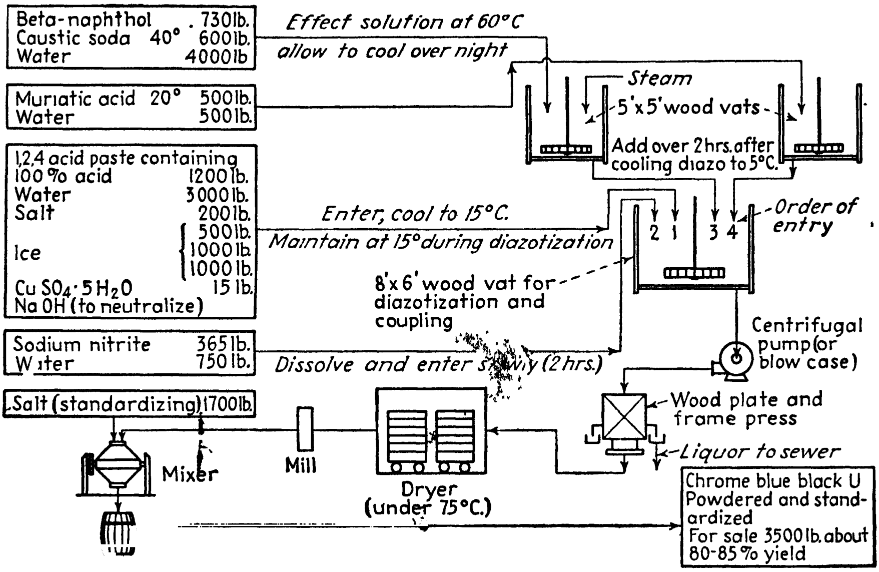

FIG. 15.—Flow sheet for Chrome Blue Black U. Monoazo or chrome dye; batch = 5 lb. moles.

Among the monoazo dyes, *Chrome Blue Black U*[2] ranks as one of the important chrome colors on wool for men's wear, particularly as its various qualities of fastness are very good (fastness to light, acids, alkalies, carbonizing, ironing, washing, perspiration, etc.). The U.S. Tariff Commission reports annual sales of over 1,700,000 lb. It is sold for a low price because of the cheapness of the raw materials and the skill of the dyemakers. The two intermediates are 1,2,4 acid (1-amino-2-naphthol-4-sulfonic acid) and β-naphthol. It might seem easy to make but in this case the nitrous acid not only diazotizes the —NH_2 group but tends to oxidize the 1,2,4 acid to tars and thus throw off the shade of the finished dye and decrease the yield. This can be avoided by diazotizing 1-amino-naphthalene-2,4-disulfonic acid and then replacing the 2-sulfonic acid by —OH through caustic soda, or by diazotizing in the presence of a zinc salt.[1] However, the oxidizing influence of the nitrous acid is diminished in the presence of a small amount of a copper salt.[2] The flow sheet, Fig. 15, follows this procedure[3] and carries out the reaction:

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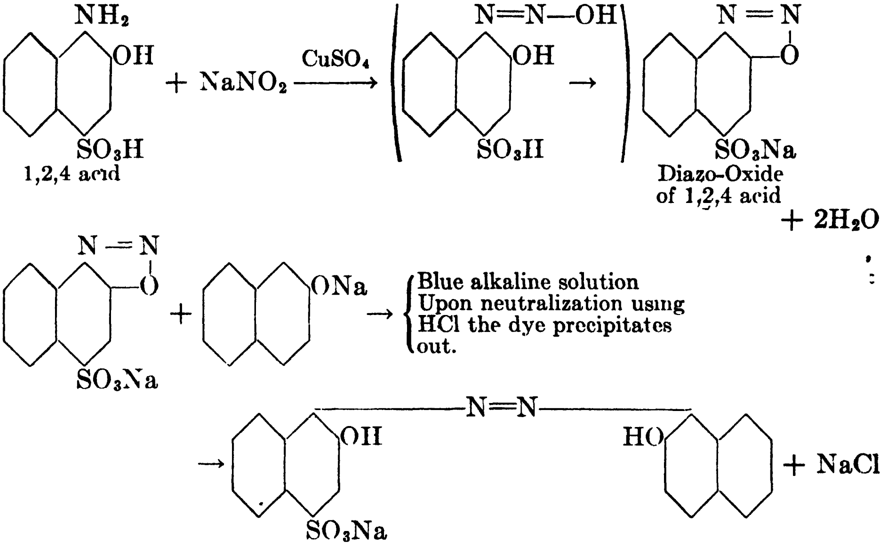
[1] *Cf.* PERRY, *op. cit.*, p. 1556.

[2] This is C.I. 202 and, like most other dyes, is sold under many names, frequently one for each manufacturer: Eriochrome Blue Black R(Gy), Calcochrome Blue Black (CCC), Pontochrome Blue Black R (DuP), Superchrome Blue B Ex (NAC). The initials in parentheses are those of the manufacturer, *e.g.*, DuP stands for Du Pont. See also dye lists in the yearbooks of the American Association of Textile Chemists and Colorists.



Chrome Blue Black U

As in all diazotizations and couplings, tests must be made toward the end of the reaction. In this case, after stirring for a while, a sample diluted with an equal volume of distilled water should dissolve and show only a slight excess of nitrous acid when tested with starch iodide paper.[4] The diazo oxide of the 1,2,4 acid is a suspension of bronze crystals which can be filtered off. However, this is not usually considered necessary, and the coupling is carried out next morning after reducing the tempera-

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[1] *Cf.*, Rowe, *op. cit.*, C.I. 202, where methods and references are given.

[2] Saunders, *op. cit.*, p. 7; Geigy, U.S. Pat., 793743 and English Pat., 10234 (1904).

[3] Saunders, *op. cit.*, pp. 7, 180; O'Brien, *op. cit.*, pp. 151–154.

[4] U.S. Pat., 2160882 (1939) by Lubs describes a new and novel method for removal of excess nitrous acid, using sulfamic acid and thus avoiding side reactions which adversely affect the purity of the color of the dye.

TABLE 6.—IMPORTANT AZO DYES

Colour Index No.	Name and class of dye	Intermediates from which dye is made	Dye application class
	Monoazo dyes: containing R—N=N—R′		
20	Chrysoidine Y	Aniline *m*-Phenylenediamine	B
24	Sudan I	Aniline β-Naphthol	SS
138	Metanil Yellow	Metanilic acid Diphenylamine	A
142	Methyl Orange	Sulfanilic acid Dimethyl-aniline	A[1]
151	Orange II	Sulfanilic acid β-Naphthol	A
202	Chrome Blue Black U	1-Amino-2-naphthol-4-sulfonic acid β-Naphthol	M
	Disazo dyes: containing R—N=N—X—N=N—R′		
246	Acid Black 10B (Naphthol Blue Black)	*p*-Nitro-aniline H acid	A
332	Bismarck Brown 2R	*m*-Tolylenediamine (3 moles)	B
401	Developed Black BHN	Benzidine 2-Amino-8-naphthol-6-sulfonic acid (alk.) 1-Amino-8-naphthol-3,6-disulfonic acid (alk.)	D
406	Direct Blue 2B	Benzidine 1-Amino-8-naphthol-3,6-disulfonic acid (alk.) (2 moles)	D
518	Direct Pure Blue 6B	Dianisidine 1-Amino-8-naphthol-2,4-disulfonic acid (alk.) (2 moles)	D
	Trisazo dyes: containing R—N=N—X—N=N—Y—N=N—R′		
593	Direct Green B	Benzidine Phenol 1-Amino-8-naphthol-3,6-disulfonic acid *p*-Nitro-aniline	D

[1] Indicator.

NOTE: In this table A stands for acid dye, B for basic dye, D for direct dye, M for mordant dye, S for sulfur dye, SS for spirit-soluble dye, and V for vat dye.

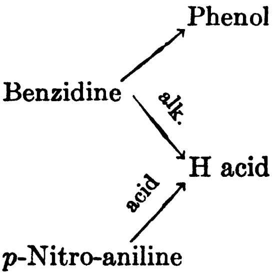
ture to 5°C. by adding about 1,000 lb. of ice. The coupling is then effected by running in the sodium naphthol solution slowly over 2 hr. The blue alkaline solution of the dye is precipitated the next day with diluted muriatic acid, testing toward the end so as to leave the mother liquor faintly acid to Congo red test paper. The usual product sold, except for the higher priced concentrates, contains salt about equal to the dye contents.[1]

From the flow sheet and current material prices, the cost of the materials[2] for Chrome Blue Black can be calculated, to which should be added:

	Per 100 Lb. of Standardized Dye
Productive labor	$2 00
Nonproductive labor	0 75
Power and steam	1 25
Maintenance and repairs	1 35
Supplies	0 55
Plant overhead	1 30
	$7 20

This figure should be increased by pro rata charges for depreciation, taxes, insurance, and sales expense.

Directions for making other dyes can be found in the references at the end of this chapter.[3] The apparently complicated trisazo dye, *Direct Green B*, C.I. 593, is made from four intermediates according to the scheme:



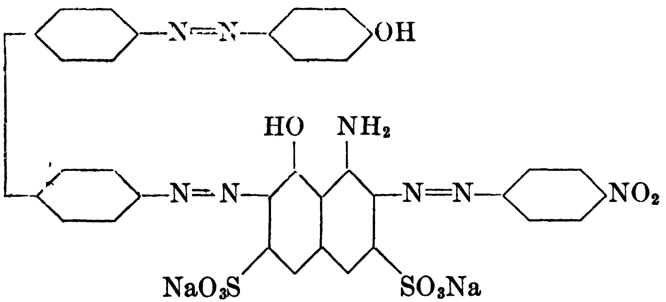
The arrows indicate coupling from diazo body to a hydroxy or amino derivative. The resulting dye formula is

---

[1] Most dyes contain salt or sodium sulfate to standardize, since batches will not come from the plant in exactly the same strength. This is adjusted by a harmless diluent. Very pure dyes are such products as the food, medicinal, or bacteriological dyes, which are costly compared with the low-priced textile dyes.

[2] A flow sheet with costs for 1,2,4 acid is given on pp. 1111 and 1114 in the chapter on Dyes, by Shreve, in "Rogers' Manual of Industrial Chemistry." This dye is sold so cheaply that even the 1,2,4 acid would have to be manufactured to compete.

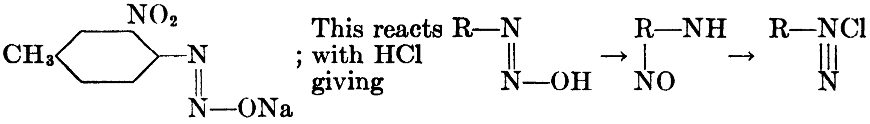
[3] Particularly in Rowe, "Colour Index and Supplement." A flow sheet for C.I. 518, Direct Pure Blue 6B or Diamine Sky Blue FF, is given by Woodward, in Groggins, *op. cit.*, p. 149. *Cf.* O'Brien, *op. cit.*



Direct Green B

In 1880 the making of an azo dye, *Para Red,* C.I. 44, right on the fiber was undertaken. This was done by padding the cotton cloth with an alkaline β-naphthol solution, followed by an acid solution of diazotized *p*-nitro-aniline. Later the β-naphthol was replaced by the more stable β-naphthoic acid (3-hydroxy-2-naphthoic acid) or its anilide (Naphthol AS). This generalized process enabled the more soluble constituents to penetrate into the fiber and there to form the insoluble azo dye. Such procedures are still very important and comprise a good share[1] of those made-on fiber dyes, now known as *azoics.*

This procedure required the dyer to be also a dyemaker. To obviate this and to give the consumer through the dyer an improved line, particularly for printing on cotton, the *stabilized* azoics have been made. These are azo dyes and may be defined as "a mixture of a soluble stabilized aromatic diazo compound and a secondary component with which it can couple under suitable conditions to form an insoluble colored pigment."[2] These are sold under the use class names of *Rapid Fast* or *Pontagen* for the azoics, consisting of mixtures of various diazo bodies stabilized by conversion into a "nitrosamine" and various hydroxy-naphthoic acid anilides.[3] The nitrosamines are made by the action of strong caustic soda on a diazo, such as that from *m*-nitro-*p*-toluidine, which may be formulated:



anti-Diazotate

; This reacts with HCl giving

$$R{-}N{=}N{-}OH \rightarrow R{-}NH{-}NO \rightarrow R{-}N{\equiv}N\,Cl$$

Nitrosamine

Diazonium salt

The dye is developed on the fiber by making the mixture slightly acid.

---

[1] The U.S. Tariff Commission reported sales of Naphthol AS as over 700,000 lb. out of over 3,000,000 for the total azoic group.

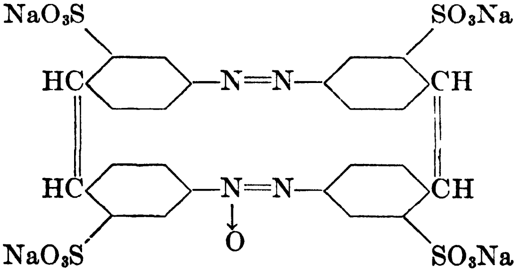
[2] LUBS, Stabilized Azoic Colors, *Am. Dyestuff Reptr.,* **26,** 101 (1937). *Cf.* DORMAN, Naphthol AS Type Dyes, *Am. Dyestuff Reptr.,* **28,** 79 (1939).

[3] C.I. 70; WOODWARD, in Groggins, *op. cit.,* pp. 116–118.

Among other stabilized azoics the Diagens of the Du Pont Company and the Rapidogens of the General Dyestuffs Corporation are outstanding developments of the past few years[1] for printing on cotton goods with results of good fastness and at a reasonable price. The diazo is stabilized by combination with a secondary amine containing a solubilizing group. This gives a perfectly stable mixture with the other compound, usually a naphthol AS anilide derivative (derivative of anilide of 3-hydroxy-2-naphthoic acid), as long as in alkaline condition. The constituents react and form the insoluble azo dye when acidified, as exemplified in the reactions shown on page 886.

For years, metallic salts, particularly of chromium and of aluminum, have been used in making lakes and as mordants. Recently Crossley and Shafer[2] of the Calco Chemical Division of the American Cyanamid Company, have brought out a new class of colors, the *metallized dyes*, sold under the name *Calcofast.* These dye wool from acid baths with excellent fastness to washing, milling, and light. Examples[3] are Calcofast Olive Brown G, Calcofast Orange 4R, and Calcofast Orange YF made by coupling nitro-diazo-phenols with phenyl-methyl-pyrazolones in weakly acid solution and then metallized by reacting at the boil with the desired metallic salt. The metal used may vary over a wide range, or a combination of metals may be employed yielding different colors. The metal derivatives are soluble and are a part of the molecule. The metallized dye is obtained by salting out the reaction liquor using common salt up to 25 per cent of the aqueous solution.

Stilbene Dyes.—Chromophores: —N=N— and =C=C=. These dyes are sometimes classed with the azo group to which they are closely related. Although this class of dyes contains an azo chromophore, it is not made by the diazotization and coupling reactions. These are *direct* cotton dyes and the most used example is *Direct Yellow R,* C.I. 620, whose formula is



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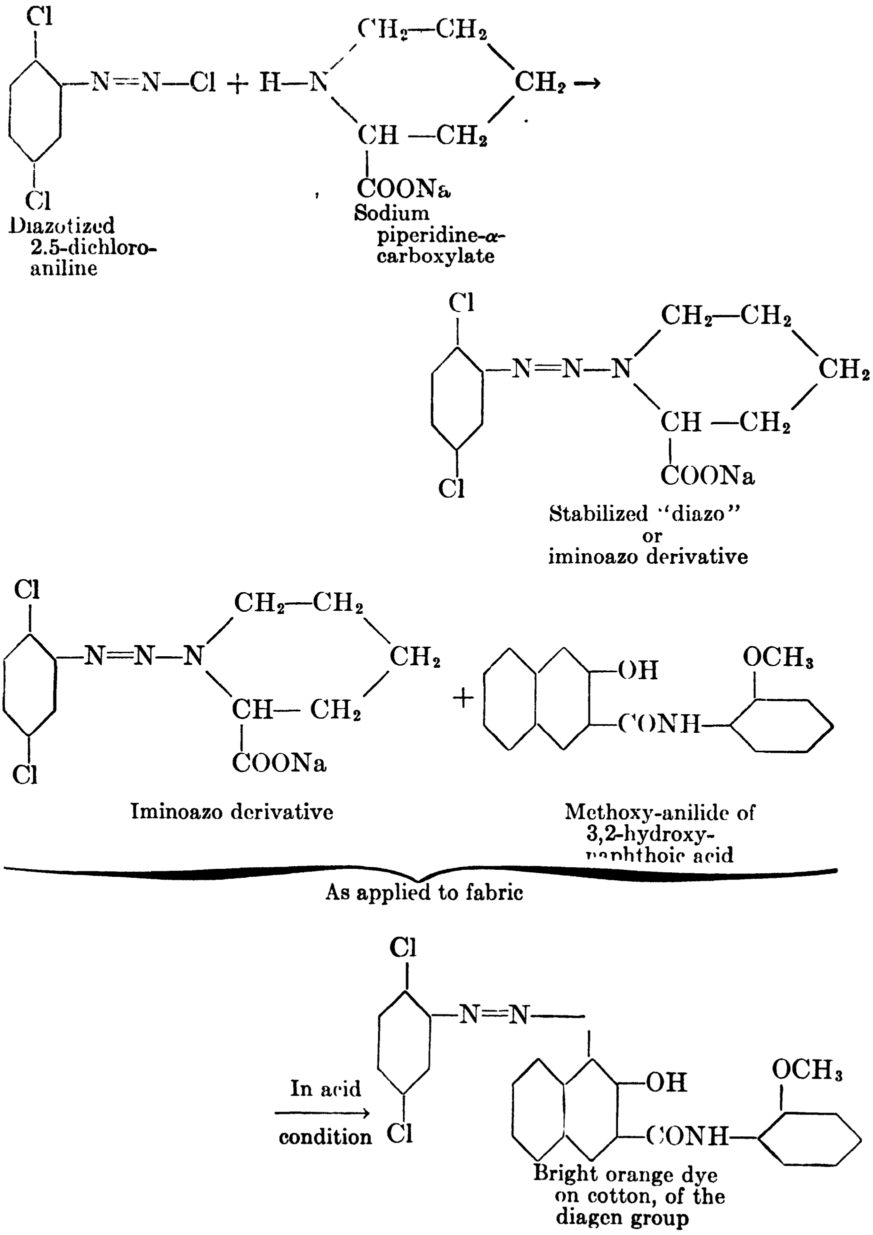
[1] Lubs, *op. cit.;* Dorman, *op. cit.;* Dahlen, U.S. Pats., 1968878 (1934) and 2008750 (1935); Dahlen and Zwilgmeyer, U.S. Pat., 2021911 (1935).

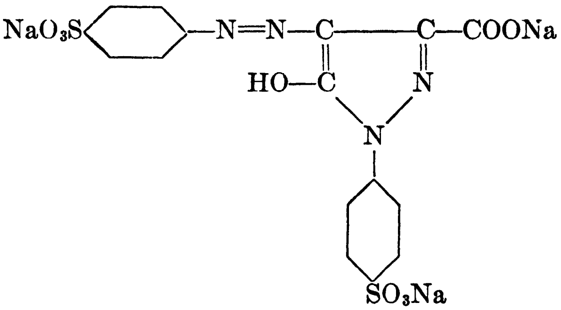
[2] Crossley and Shafer, U.S. Pats., 2034390 (1936), 2086854 (1937), 2120799 (1938), 2136650 (1938), 2213647 (1940), 2220396 (1940), 2220397 (1940).

[3] U.S. Pat. 2120799 (1938). Specific examples are given.

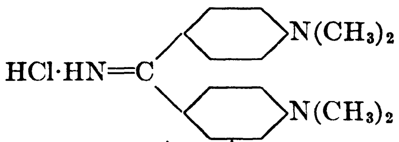

Diazotized 2.5-dichloroaniline
Sodium piperidine-α-carboxylate
Stabilized "diazo" or iminoazo derivative
Iminoazo derivative
Methoxy-anilide of 3,2-hydroxy-naphthoic acid
As applied to fabric
In acid condition
Bright orange dye on cotton, of the diagen group

This dye is made by the action of heat and caustic soda on *p*-nitrotoluene-*o*-sulfonic acid (4 moles).

Pyrazolone Dyes.—Chromophores: —N═N— and ═C═C═. These are also sometimes classed with the azo group. The members are acid dyes and are usually used on silk and wool, though to some extent for lakes. The chief member is *Tartrazine,* C.I. 640, which is made from dioxytartaric acid and phenylhydrazine-*p*-sulfonic acid (2 moles). Its formula is

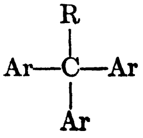


Ketonimine Dyes.—Chromophore: —NH═C═. This small class (2 members) is so close to the next, or triarylmethane dyes, that these two dyes are frequently grouped with the triarylmethane ones. The members are *Auramine,* C.I. 655, and its homolog. These are *basic* dyes and are largely used on cotton mordanted with tannin and tartar emetic. Auramine is made from dimethyl-aniline (2 moles) and phosgene, giving Michler's ketone directly (tetramethyldiamino-benzophenone) which is aminated by heating with ammonium chloride and salt in a current of ammonia. There results:



Auramine

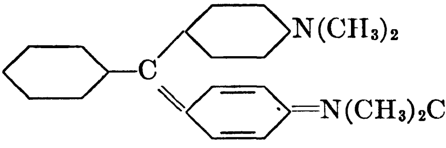
Triarylmethane Dyes.—Chromophores: ═C═NH and ═C═N—. However, the cause of color in this large and important class with the



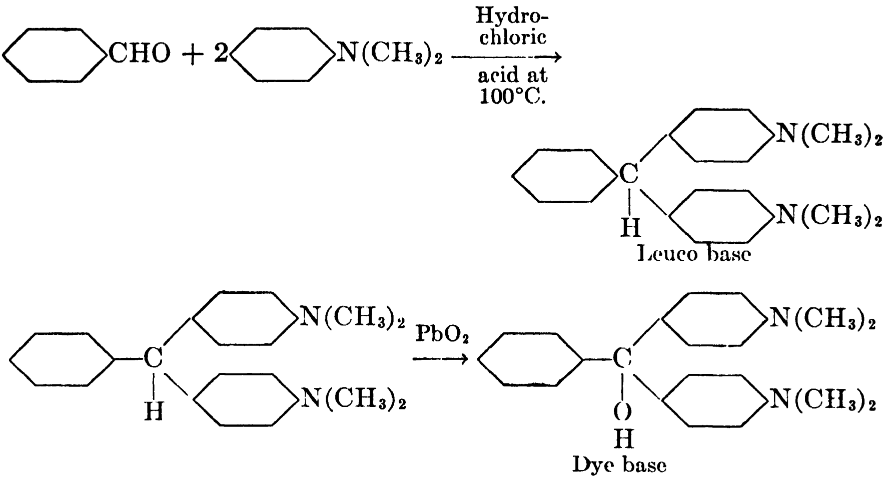
$$Ar—\overset{\displaystyle R}{\underset{\displaystyle Ar}{C}}—Ar$$

complex as the characteristic chemical group, is due to more than the presence of a simple chromophore. Conjugated bonds, unsaturation, and quinoid arrangement are all important, but it may be that resonating structure is the basic explanation.[1] These dyes are basic ones, dyeing cotton with tannin mordant, or when sulfonated, acid dyes for wool and silk. They furnish very beautiful shades but, for the most part, they are not very fast to light.

Malachite Green, C.I. 657, is the chloride of *p,p'*-tetramethyldiamino-triphenylcarbinol,[2] sold usually as zinc chloride complex. Its formula is



This dye is made by condensation of benzaldehyde and 2 moles of dimethyl-aniline with the aid of heat and hydrochloric acid. This furnishes tetramethyldiamino-triphenylmethane, called the *leuco* base, which is then oxidized by lead peroxide to the *dye base,* the salt of which is the commercial dye (either oxalate or zinc double chloride).



Many of the triarylmethane dyes are carried through this same sequence.

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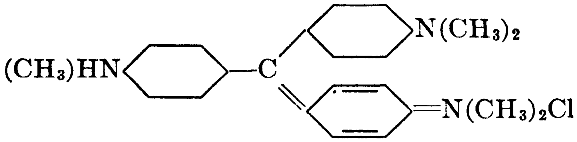
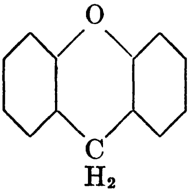
[1] *Cf.* LEWIS and CALVIN, *op. cit.* The influence of alkylation in color change is tabulated by Shreve, p. 508, in Groggins, *op. cit.*

[2] This is the nomenclature found in the dye books. Chemical Abstracts names these dyes by the more logical I.U.C. system and would call the dye base of which commercial Malachite Green is a salt, bis (*p*-dimethylaminophenyl)-phenylmethanol.

Methyl Violet, C.I. 680, is a basic dye, sold to the extent of more than 1,000,000 lb. per year and for a wide variety of uses, *e.g.*, on cotton, silk and paper as a self color, in calico and silk printing, in the dyeing of jute, coco fiber, wood, linen, straw, leather, and in the manufacture of marking and stamping inks, carbon papers, copying pencils, and lacquers. This dye is the hydrochloride of pentamethyltriamino-triphenyl-carbinol. It is made by the oxidation of dimethyl-aniline (3 moles) using cupric chloride in the presence of phenol. One methyl group goes to formaldehyde which supplies the central carbon.[1] The function of the phenol in this reaction is unknown. The Methyl Violet has the formula:



Xanthene Dyes.—These dyes usually are derivatives of xanthene.



It is difficult to say what the chromophore is, but the remarks as to the cause of color in the triaryl group are of value here. These dyes are quite closely related to the aryl methane ones, and the oxygen bridge can be viewed as made by the elimination of water from two hydroxyl groups, ortho to the carbon bridge. The presence of conjugation is characteristic of such chromophores as $=C=O$ or $=C=N-$. This class contains the useful indicator: phenolphthalein,[2] C.I. 764, which, however, lacks the xanthene oxygen bridge. The most widely sold of these dyes is *Eosin*, C.I. 768, which is tetrabromofluorescein. Fluorescein is made by condensation of resorcinol (2 moles) and phthalic anhydride in presence of a dehydrating agent such as zinc chloride. The formula of Eosin is shown on page 890. Eosin is an acid dye for wool and silk, and also for cotton with a tin or alum mordant. However, its chief application is to make lakes and for the preparation of ordinary red writing and stamping inks.

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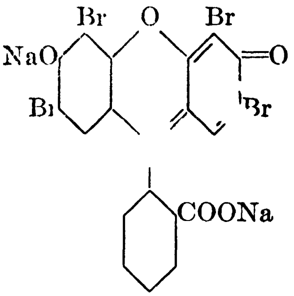
[1] Details of these various processes and the merchandising of the reactions as far as they are published can be obtained from the references at the end of this chapter. The "Colour Index and Supplement" and the book by Georgievics and Grandmougin are the best general references.

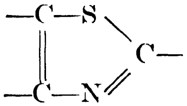
[2] As phenolphthalein is more important in fields other than dyes, it is considered in Chap. XXXIX.



Eosin
C.I. 768

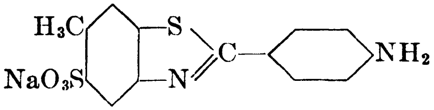
Tetraiodo-phenolphthalein sodium, or *Iodeikon*, is an important medicinal dye employed for visualization of the gall bladder, where its iodine content makes it opaque to X rays, thus showing gallstones by contrast, or enabling the discharge or functioning of the gall bladder to be followed.

Thiazole Dyes, or Primuline Dyes.—These contain sulfur in the thiazole ring:

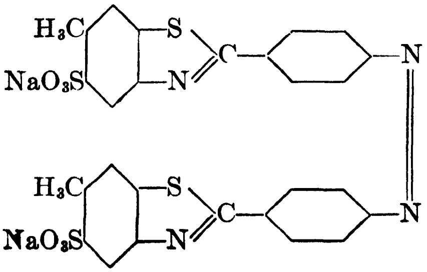


The chromophores are $>C{=}N-$ as well as the $-S-C\equiv$ etc., but the arrangement in conjugated double bonds is of importance. These dyes are chiefly direct or developed dyes for cotton, though some of them are union dyes.

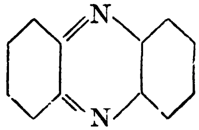
Direct Fast Yellow, C.I. 814, is a direct color of excellent properties; it is also a union dye. It is made by sodium hypochlorite oxidation of the sodium salt of dehydrothio-*p*-toluidine-sulfonic acid.



This latter is prepared by heating *p*-toluidine and sulfur followed by sulfonation. Direct Fast Yellow has also an azo chromophore, as is shown by the following structure:

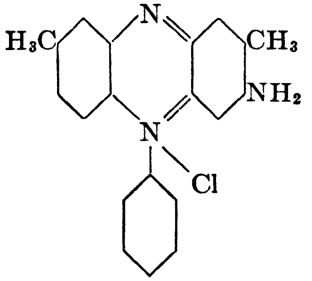


Azine Dyes.—The azine dyes have as a mother substance phenazine:

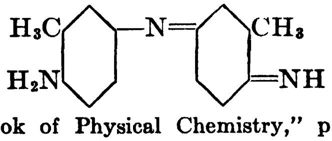


and we may assume as chromophores >C=N—; but here, as in many other of these complicated ring systems, resonance is being more and more looked upon as the basis of color. Indeed in these simpler chromophores like >C=N— the structure contains a "fairly loosely bound chromophoric electron."[1] The azine dyes are quite varied in their application. The *Nigrosines*, C.I. 864 and 865, have annual sales of over 2,600,000 lb. and are used, after jetting with suitable yellow dyes, for blue-black and black polishes for leather shoes and other leather goods. Their ultimate constitution is unknown. The nigrosines are also employed for silk dyeing. They are such good dyes at such reasonable prices, that a welcome addition is *Microsol Black*,[2] a black pigment insoluble in water and substantially insoluble in acetone, alcohols, and hydrocarbons. This black pigment, which gives a gray upon dilution, is useful for coloring lacquers, plastics, paints, inks, and emulsions for textile printing. It is made by treating spirit-soluble or unsulfonated nigrosine (or induline) with an oxidizing agent such as manganese dioxide or nitric acid.

Although *Safranine*, C.I. 841, is not sold so largely as the nigrosines, its constitution is simple and it may be formulated:



It is made[3] by oxidation by CrO_3 in acetic acid of equimolecular proportions of *p*-tolylenediamine and *o*-toluidine to the indamine:



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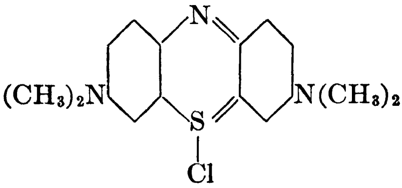
[1] Glasstone, "Textbook of Physical Chemistry," p. 573, D. Van Nostrand Company, Inc., New York, 1940.

[2] Friese (American Cyanamid Company), U.S. Pat., 2194423 (1940).

[3] *Cf.* Fierz-David, "Dye Chemistry," pp. 178*ff*., Churchill, London, 1921.

This is then condensed with aniline (or *o*-toluidine) in the presence of an oxidant. Safranine is a basic dye and is used largely on cotton mordanted with tannin and fixed with tartar emetic.

Thiazine Dyes.—These have the important member, *Methylene Blue,* C.I. 922, which has the formula:

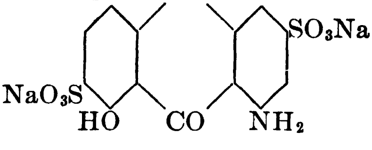


This is a basic dye and is made from dimethyl-aniline and sulfur.

Sulfur or Sulfide Dyes.—These dyes are so complex that very little is known of their chemical structure. The chromophores present are $\equiv C-S-C\equiv$ and $\equiv C-S-S-C\equiv$ as bridges in complicated molecules.[1] These sulfur dyes are used to dye cotton from a sodium sulfide bath in dull but full shades of excellent fastness.

Sulfur Black, C.I. 978, is the most widely sold of all dyes figuring on a dry basis, the sales amounting to over 5,000 tons annually. It is also a very low priced product. Sulfur black is made from either dinitro-chlorobenzene or dinitro-phenol by refluxing with a polysulfide solution for many hours followed by precipitation of the dye by air oxidation. The demand for sulfur black was responsible for the first plant in America to produce chloro-benzene, installed about 1915. The time for thionation in some of these sulfur colors can be much shortened—from days to hours—by changing the solvent from alcohol or water to a monoalkyl ether of diethylene glycol.[2]

Anthraquinone Dyes.—Chromophores: $=C=O$ and $=C=C=$ arranged in the anthraquinone complex. The auxochromes are frequently (1) —OH when the dyes fall into the mordant class like Alizarin, C.I. 1027, or (2) $-SO_3H$ when we have, for example, the acid dye *Acid Alizarin Blue B,* C.I. 1054. These dyes have very fast characteristics. Acid Alizarin Blue has the formula:



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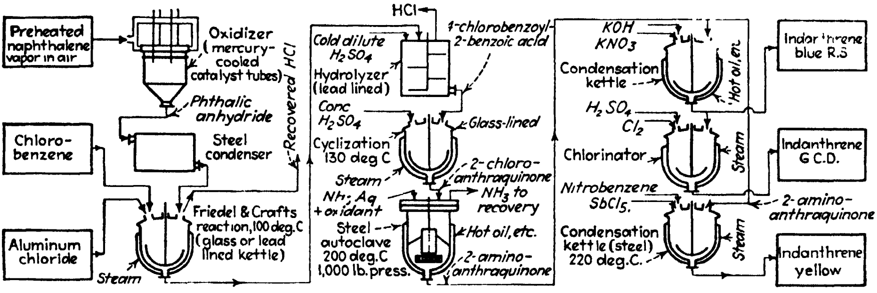
[1] Empirical formulas are variously given as $C_{24}H_{16}N_6O_8S_7$ or $C_{24}H_{16}N_6O_8S_8$ for typical sulfur dyes.

[2] LUBS and STROUSE, U.S. Pat., 1944250 (1934).

and is manufactured by forming the 1,5-dihydroxy-anthraquinone (anthrarufin) followed by nitration, sulfonation, and reduction.

Anthraquinone Vat Dyes.—These are also based on anthraquinone like the preceding class and have many of the chromophore and the fastness characteristics of that class, only accentuated in many instances. However, these dyes are capable of being reduced to an alkaline soluble derivative which is called a *vat* and which oxidizes to the color (thus resembling the next class or indigo dyes). To make a commercial dye the reduced or leuco compound must have affinity for the fiber, and the insoluble dye must adhere firmly.[1] These necessities are met with in so many of the members of this class that we have in the vat dyes a rapidly growing class of colors of remarkable properties of fastness and permanency. Their growth has been greatly stimulated, indeed made possible, by the American discovery or commercialization of synthetic phthalic anhydride from air oxidation of naphthalene, from which synthetic anthraquinone is manufactured. These vat dyes are employed largely on cotton and rayon and, to a limited extent, on silk; indeed they furnish us some of our finest and *fastest* colored fabrics. Figure 16 summarizes



Phthalic anhydride	148 lb.	To produce 235 lb. 2-chloroanthraquinone
Chlorobenzene (80% recd)	600 lb.	
Aluminum chloride	300 lb.	
H_2SO_4 (100 per cent)	1,500 lb.	

2-chloroanthraquinone	235 lb	To produce 200 lb 2-aminoanthraquinone
NH_3 (28 per cent)**	1,500 lb.	

2-aminoanthraquinone	200 lb	Indanthrene yellow G No. 1118
Nitrobenzene*	2,000 lb.	
Antimony pentachloride	700 lb.	

2-aminoanthraquinone	200 lb.	Indanthrene blue R.S No 11[illegible] (60-65 lb 100% dye)
Caustic potash	1,000 lb.	
KNO_3 (or K-chlorate)	40 lb.	

*Recovered as aniline or nitrobenzine

Indanthrene blue RS	100 lb.	Indanthrene blue G C D No 1113 (about 110 lb. 100% dye)
H_2SO_4 (93%)	1,200 lb.	
$FeSO_4$	90 lb.	
Cl_2	25 lb	

**90% recoverable

FIG. 16.—Outline flow sheets for simple vat dyes—many steps omitted.

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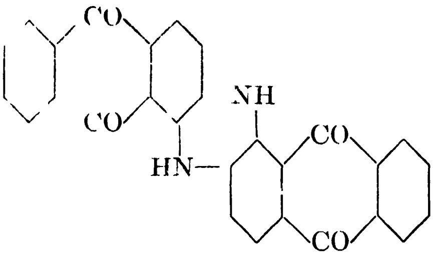
[1] The basic chemical structure that gives to an anthraquinone or indigoid dye the vat dyeing characteristics is usually the presence of two CO groups which on reduction give alkali-soluble C(OH) groups.

The almost invariably used reducing agent is sodium hydrosulfite, $Na_2S_2O_4$, employed for solutions; or the formaldehyde compound, formaldehyde sulfoxalate employed for printing. The reaction may be expressed:

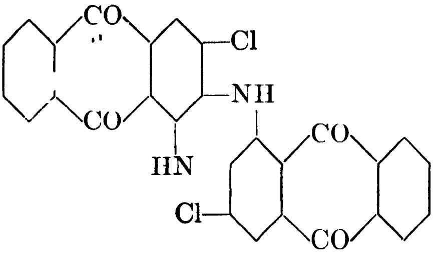
$$Na_2S_2O_4 + 2NaOH + H_2O = Na_2SO_4 + Na_2SO_3 + 2H_2 \text{ (on the dye)}$$

Recently Lubs has patented in U.S. 2164930 (1939) the use of the hydrogen peroxide oxidation product of thiourea for the same purpose.

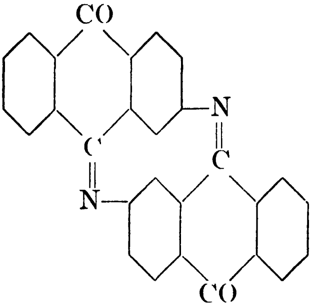
the flow sheets depicting in outline the sequences from main raw materials to the following three vat dye



Indanthrene Blue RS,
C I 1106



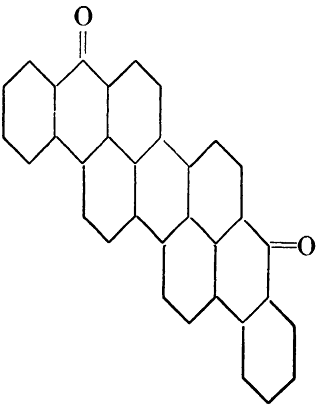
Indanthrene Blue GCD,
C.I. 1113



Indanthrene Yellow G,
C I 1118, or
Flavanthrene

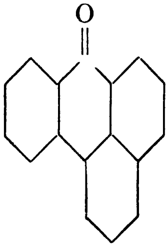
These dyes all need β-amino-anthraquinone as an essential intermediate, proceeding by an oxidizing condensation to the dyes. Indanthrene Blue GCD is a chlorination product.

Another example of these very fast and stable vat dyes is *Anthraquinone Vat Dark Blue BO,* C.I. 1099 (also sold as Hydroform Deep Blue BOA as well as under other names), which has the structure:

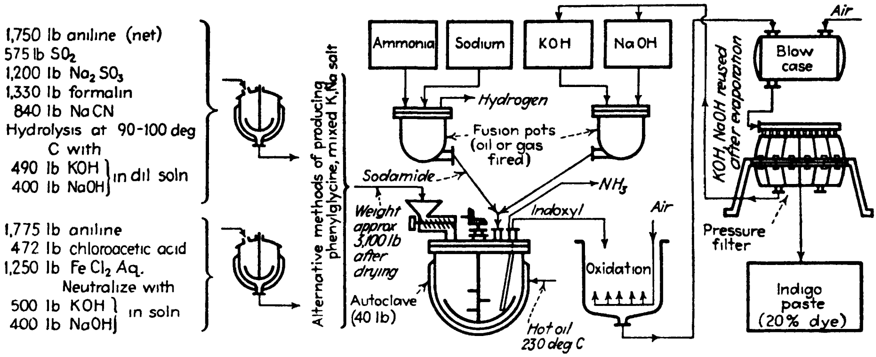


or $C_{34}H_{10}O_2$

This is a very compact molecule, consisting very largely of carbon (nearly 90 per cent, and possessing great stability. It is made by caustic-potash fusion from benzanthrone.



The benzanthrone is manufactured by condensation from anthranol and glycerine under the influence of sulfuric acid, and the anthranol in turn from anthraquinone by reduction with sulfuric acid and iron (or copper).

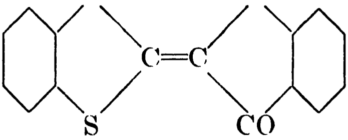


Phenylglycine (K, Na)	3100 lb.	Sodium	860 lb	Per ton Indigo 100% or 5 tons 20% paste
KOH (recovered)	3,050 lb	Ammonia	630 lb	
Na OH (recovered)	2400 lb.			

Note Yields 80-82% on aniline, KOH, NaOH, NH_3 recovered and reused

FIG. 17.—Outline flow sheet for indigo.

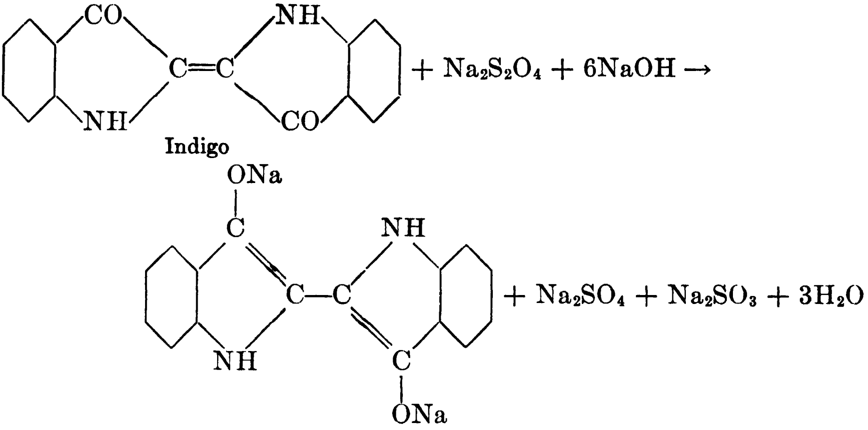
Indigoid Dyes.—The remarks that headed the vat dyes section pertain largely to this chemical class also, except that the members of this class are derivatives of indigo or thioindigo.



Thioindigo, 1207

These dyes fall in the vat use classification and are applied principally on cotton. A very large tonnage of indigo is manufactured each year. Recently this has amounted to over 6,000 tons annually of 20 per cent paste. When the oriental export business was flourishing, production up to 15,000 tons were made. Indigo was first a naturally cultivated dye, but the German chemists worked out a profitable synthesis for indigo, though only after spending over $6,000,000 in research and development. However, this was a profitable venture for them as their synthetic indigo was more uniform and much cheaper than that previously grown on 1,500,000 acres, principally in India.

Indigo, C.I. 1177 itself is a water-insoluble blue dye of good properties, largely used on cotton and rayon, but sometimes on silk. When dyeing, it is reduced by hydrosulfite to make the alkali soluble leuco derivative or indigo white.

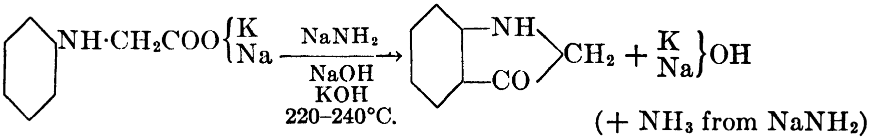


Indigo

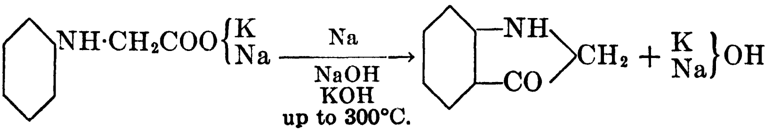
Indigo white

Figure 17 gives an outline flow sheet for the manufacture of indigo by several sequences from aniline, which is the present commercial starting point for the intermediate product, phenylglycine. The following reactions summarize the chemical changes involved in this flow sheet (*cf.* also Fig. 14).

Indoxyl Using Sodium Amide:

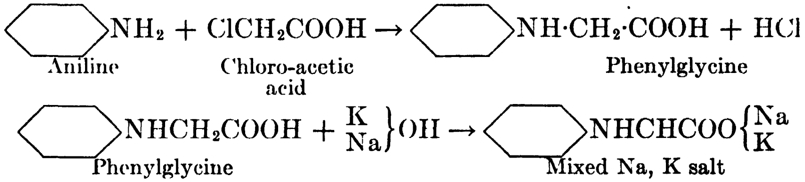


Indoxyl Using Metallic Sodium:

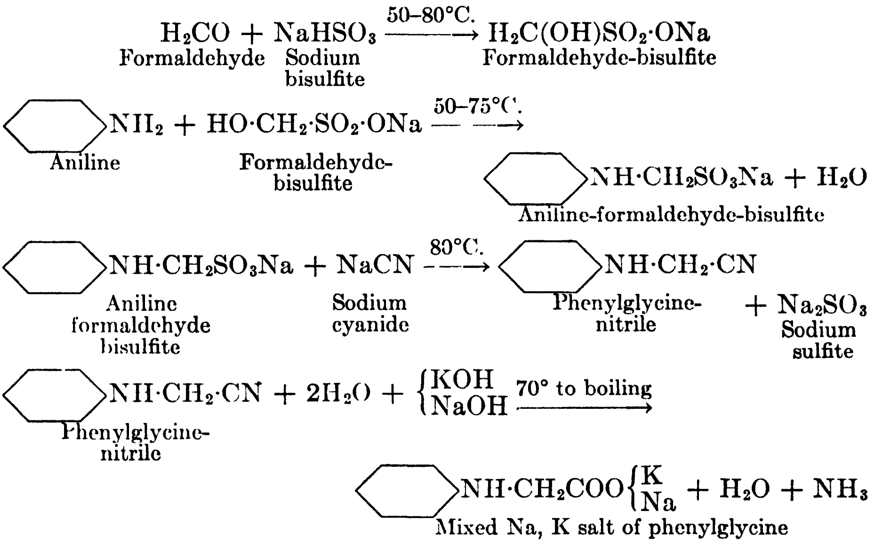


Although, apparently, the sodium amide or the metallic sodium does not enter into the reaction, these two reagents and the mixed NaOH and KOH maintain the necessary fluxing and anhydrous condition for the dehydrating ring closure to proceed with good yields. The use of the *mixed* Na, K salt of phenylglycine and of *mixed* NaOH, KOH gives lower fusions points with consequent lower temperatures and enhanced yields.

Phenylglycine by Chloro-acetic Acid:



Phenylglycine by Formaldehyde and Sodium Cyanide:


H₂CO + NaHSO₃ 50–80°C. → H₂C(OH)SO₂·ONa
Formaldehyde
Sodium bisulfite
Formaldehyde-bisulfite
NH₂ + HO·CH₂·SO₂·ONa 50–75°C. →
Aniline
Formaldehyde-bisulfite
NH·CH₂SO₃Na + H₂O
Aniline-formaldehyde-bisulfite
NH·CH₂SO₃Na + NaCN 80°C. →
NH·CH₂·CN
Aniline formaldehyde bisulfite
Sodium cyanide
Phenylglycine-nitrile
+ Na₂SO₃
Sodium sulfite
NH·CH₂·CN + 2H₂O + {KOH NaOH 70° to boiling →
Phenylglycine-nitrile
NH·CH₂COO{K Na + H₂O + NH₃
Mixed Na, K salt of phenylglycine

Phthalocyanine Dyes and Pigments.—Figure 19 represents the structure of copper phthalocyanine. This group is the most recent introduction to the family of dyes. In fact here is the first new class[1] of synthetic dyes in many years. This new group contains a new chromophore of great complexity, or more likely a new arrangement of the simpler chromophores: =C=N— and =C=C=. Here again, it may be that resonance will be shown to be the fundamental cause of the color. In copper phthalocyanine four isoindole units are linked by four nitrogen atoms and one copper atom to furnish a complicated ring structure which, however, may be viewed as somewhat similar to the basic ring system of chlorophyll. This ring system and its derivatives show remarkable stability[1] to light, water, chemicals and even heat. They sublime unchanged at 550°C. Because of this stability, their insolubility in water, and the intensity and beauty of their color, these phthalocyanines are of particular applicability to the pigment and paint fields. Three of these blue-green pigments have become important commercially: The metal-free phthalocyanine is sold as *Monastral Fast Blue GS* powder (Du Pont) and also as aqueous pastes and dispersions. The copper derivative is merchandised as a practically pure powder as *Monastral Fast Blue BSN* powder.

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[1] Dahlen, The Phthalocyanines, *Ind. Eng. Chem.*, **31,** 839 (1939). This article includes a bibliography of the work, gives patents, and describes the fundamental and enlightening studies of R. P. Linstead of England.

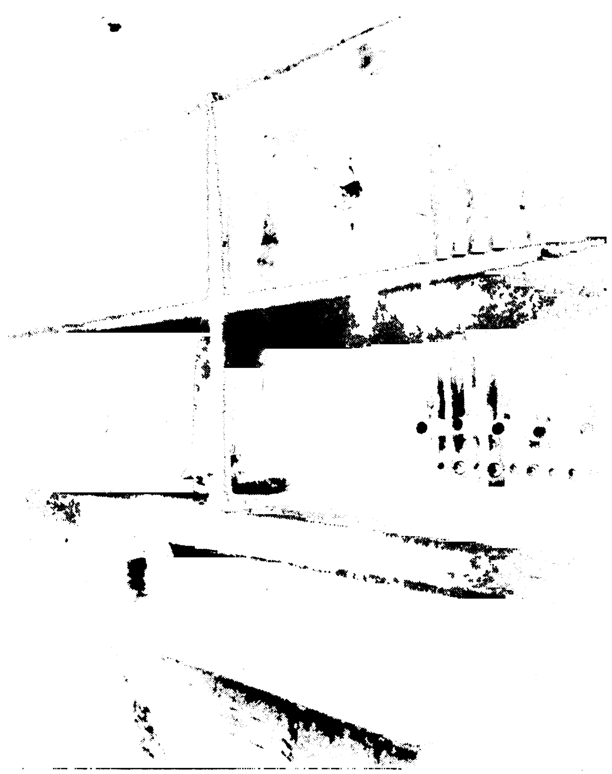

FIG. 18—Indigo paste being removed from plate-and-frame filter press at the Du Pont Dye Works at Deepwater Point, N.J. (*Courtesy of E. I. du Pont de Nemours & Company, Inc.*)

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[1] SCHWARZ, The Phthalocyanines Are Faster than Anything in Color Produced So Far, *Am. Dyestuff Reptr.*, **29**, 7 (1940).

The copper phthalocyanine is highly chlorinated and is then sold as *Monastral Fast Green GS* powder and modifications. It has about 14 chlorine atoms per phthalocyanine unit. These dyes are only of the blue and green shades, but they supply a long-felt want for pigments of their excellent properties. They were discovered accidentally as an impurity in the manufacture of phthalimide. They are sold as pigments,

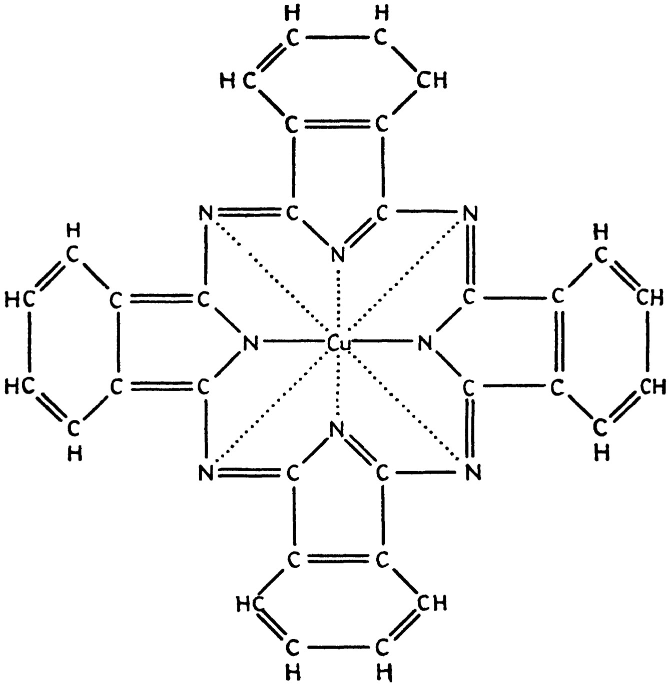
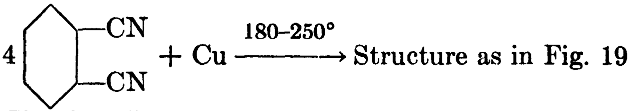


FIG. 19.—Copper phthalocyanine structure. (*After Dahlen.*)

or insoluble but highly dispersed colors, in printing inks, artists' colors, paints, lacquers, enamels, coated textiles, paper, linoleum, and rubber. We may summarize[1] their manufacture according to the following equation:



Phthalonitrile Copper Phthalocyanine (Copper)

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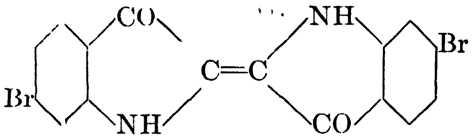
[1] Other procedures are available, such as heating the phthalonitrile with cuprous chloride, or probably better by reacting phthalic anhydride and urea in presence of cupric chloride. The crude reaction product is not suitable for dye use and must be dissolved in concentrated sulfuric acid and reprecipitated by dilution with water to obtain the physical and chemical form suitable for dyes. *Cf.* DAHLEN, *op. cit.*

Natural Organic Dyes.—For centuries these have been of the utmost importance. We have all heard of *Tyrian purple* of the ancients. It was extracted from mollusks growing on the shore of the Mediterranean. It is, however, a dye, 6,6′-dibromo-indigo, of the following formulation:



Tyrian Purple, 1248

It could be made synthetically but we have other and better products to take its place.

This replacement of the natural, or, as they have been called, *vegetable*, dyes, by their duplicates synthetically made in our factories or by better and cheaper made products is quite the usual thing. However, *logwood*,[1] C.I. 1246, in the form of chips and extract of the wood of the tree growing in Central America, has survived competition and is used extensively to give black and blue-black colors on wool and silk, mordanted with chromium or other metals. To a lesser extent fustic, cutch, and cochineal are also employed.

Inorganic Coloring Matters.—There are a great many inorganic chemicals that are used as pigments. These were considered under paints (page 484). However, khaki shades are prepared on ducks, drills, canvas, particularly for tents, cots, and such out-of-door use by soaking the cotton cloth in a solution of ferrous sulfate or ferrous acetate. The iron is converted into the hydroxide, either by an alkali or by drying, and is then oxidized by a bleaching powder solution to the darker ferric condition.

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CHAPTER XXXIX

ORGANIC CHEMICALS, NOT OTHERWISE CLASSIFIED

All in all, the manufacture of the various synthetic organic chemicals is the fastest growing and the most complex of all of the divisions of the chemical industry. Special phases of organic chemicals are presented under the respective industries as, for instance, in Chap. XXXVIII pertaining to intermediates and dyes, in Chap. XXXVII including many organics based upon petroleum, and in Chap. XXVII embracing perfumes and the flavoring industries. This chapter includes those organic chemicals which do not fall more specifically under one of the above or other headings in this book.

Historical.—The beginnings of the organic chemical industry in the United States started with the manufacture of certain medicinal compounds during the Civil War. In 1879, a small dye works was built, and by 1917 there were seven companies engaged in the manufacture of dyes and intermediates. The medicinal field had also increased. Up to 1914 many organic chemicals had been imported from Germany. The start of the First World War not only eliminated German and Swiss imports but increased the market for organic chemicals within the United States and forced a general realization of the importance of this field. The use of refinery and natural gases as raw materials for the making of organic chemicals dates back to 1922, when isopropyl alcohol was manufactured commercially from propylene gas from a petroleum refinery.

Uses and Economics.—In 1940, the production of coal-tar synthetics amounted to 805,807,000 lb. The total of noncoal-tar synthetics manufactured was 4 billion pounds, made up of approximately 2,475 different chemicals. These productions have been greatly stimulated by the Second World War, amounting to 1,533,513,000 lb. in 1943 for coal-tar synthetics and to 9,305,711,000 lb. for noncoal-tar synthetics. The usage of these compounds covers a wide range. A partial classification includes the following: dyes, medicinals, perfumes and flavors, rubber accelerators, rubber antioxidants, synthetic resins, solvents, refrigerants, detergents, antiknock and antifreeze compounds, insecticides, flotation agents, photographic chemicals, war gases, tanning agents, dry-cleaning fluids, synthetic rubbers, humectants, and vitamins. The intricate relationships among these products has been shown in the literature[1] by means of various charts. Figure 1 illustrates some of the chemicals that may be prepared from coal, air, and water. Table 1 exhibits the distribution of noncoal-tar synthetic chemicals into various types of products. Table

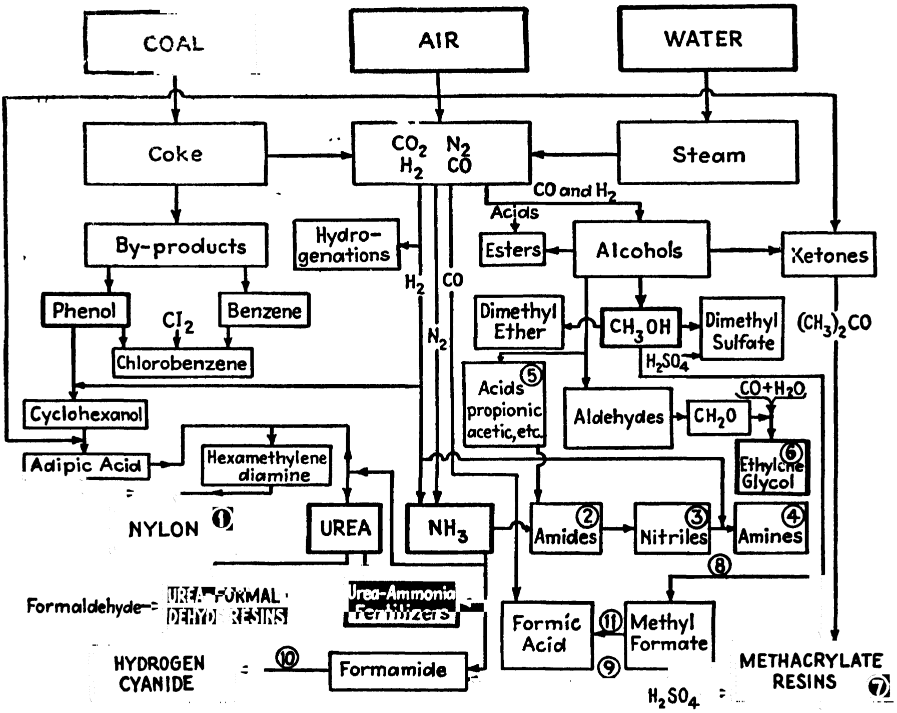

FIG. 1.—Chemicals from coal, air, and water reactions given below:

(1) For Nylon reactions see Chap. 34

(2) $RCO_2H + NH_3 \rightarrow RCONH_2 + H_2O$

(3) $RCONH_2 \rightarrow RCN + H_2O$

(4) $RCN + H_2 \rightarrow RCH_2NH_2$

(5) $CH_3OH + CO \rightarrow CH_3COOH$

(6) $CH_2O + CO + H_2O \xrightarrow[\text{pressure}]{\text{high}} COOH{\cdot}CH_2OH \xrightarrow{H_2} CH_2OH{\cdot}CH_2OH + H_2O$

(7) $CH_3COCH_3 + HCN \rightarrow \underset{\text{Acetone cyanohydrin}}{CH_3C(OH)(CH_3)CN} \xrightarrow[CH_3OH]{H_2SO_4} \underset{\text{Methyl methacrylate}}{CH_2{=}C(CH_3)CO_2CH_3} \rightarrow$
Methacrylate resin (Fig. 7, Chap. 35)

(8) $CH_3OH + CO \xrightarrow[\text{6000 lb.}]{\text{at}} HCOOCH_3$

(9) $HCOOCH_3 + NH_3 \xrightarrow[\text{100 psi}]{130°C} HCONH_2 + CH_3OH$

(10) $HCONH_2 \rightarrow HCN + H_2O$

(11) $HCOOCH_3 + H_2O \rightarrow HCOOH + CH_3OH$

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[1] ANON., Opportunities in the Synthetic Organic Chemical Industry, *Chem. & Met. Eng.* **48**, No. 10, 94(1941). The February issue every year of *Chemical & Metallurgical Engineering*, contains a most excellent statistical summary with charts and tables of all phases of the chemical industry.

2 illustrates the growth of the coal-tar synthetic organic chemical industry in the United States since 1920.

The classification of such a large number of products is naturally difficult. They might be arranged according to their origin as (1) coal-tar derivatives, (2) petroleum and natural gas derivatives, and (3) miscellaneous (such as methanol from CO and H_2) Perhaps a more modern method would be according to their manufacturing procedure; in other words, according to *unit processes.* As adopted here, this results in the following divisions for arranging the various miscellaneous organic chemicals: products resulting from nitration, esterification, amination by reduction, amination by ammonolysis, halogenation, sulfonation, hydrolysis, oxidation, hydrogenation, alkylation, and condensation. These parallel the arrangement for intermediates in Chap. XXXVIII. Since, in the preceding chapter, each unit process is broadly defined and described as to its basic chemistry, agents, and equipment, these aspects will not be repeated here. Chapter II introduces the unit processes as well as the unit operations.

NITRATION

Nitration is one of the important means for introducing nitrogen into hydrocarbons. Except for explosives and an occasional solvent, the nitro group is usually changed as by amination reduction before the product is used. Nitric acid is a powerful oxidizing agent as well as a nitrating one. Especially in difficult nitrations is much oxidation met with. Here the exact conditions for the maximum yield of nitrobodies and the minimum of oxidation products should be determined and closely adhered to.

TABLE 1.—NONCOAL-TAR SYNTHETIC ORGANIC CHEMICALS[a]

Year	Medicinals		Flavors and perfumes		Rubber chemicals		Miscellaneous	
	No. of items	Production, 1,000 lb.	No. of items	Production, 1,000 lb.	No. of items	Production, 1,000 lb.	No. of items	Production, 1,000 lb.
1929	..	.....	..	.....	..	......	245	405,186
1933	47	422	..	.....	..	......	263	767,581
1935	63	751	..	.....	..	......	302	1,591,896
1937	74	1,314	72	1,803	21	......	277	2,505,027
1939	83	1,668	94	2,137	27	13,122	318	2,984,037

[a] *Chem. & Met. Eng.*, **48**, No. 10, 96 (1941).

Probably nitro-benzene is the most important technical nitration product (Chap. XXXVIII) except for the wartime explosives such as trinitro-toluene, tetryl, picric acid, and cyclonite (Chap. XXII). The so-called *nitro-glycerine* and *nitro-cellulose* are nitrate esters (Chap. XXII).

TABLE 2.—PRODUCTION OF COAL-TAR SYNTHETIC ORGANIC CHEMICALS IN THE UNITED STATES[a]
(In thousands of pounds)

	1920	1940	Increase 1940 over 1920, per cent
Intermediates	257,727	805,807	213
Finished products:			
Dyes	88,264	127,834	45
Medicinals	5,185	18,208	250
Flavors and perfumes	266	4,490	1,964
Resins	4,660	222,943	4,684
Others	14,567	148,385	918

[a] *Chem. & Met. Eng.*, **48**, No. 10, 96 (1941).

α-Nitro-naphthalene.—In nitrating naphthalene,[1] a mixed acid of the following composition has been used: H_2SO_4, 60 per cent; HNO_3, 16 per cent. The acid is run into a jacketed cast-iron nitrator, and the finely powdered naphthalene is added while holding the temperature at 25 to 30°C. The reaction is carried out at 50°C. for 6 hr. and at 60°C. for 1 hr. At the end of this period the mass is run into a separator where the nitro-naphthalene, which floats on the surface, is removed from the spent acid. The product is washed twice with boiling water to remove acid and to steam-distill any unnitrated naphthalene. The molten product is run under agitation into cold water, producing fine pellets. If necessary, the product can be purified by recrystallization from solvent naphtha. The yield under these conditions is 95 per cent. The product is a yellow crystalline solid melting at 61°C. and is used as a dye intermediate and in further syntheses to make α-naphthylamine and dinitro-naphthalene. However, much α-naphthylamine is changed by ammonolysis into phenyl-α-naphthylamine for an antioxidant in rubber or gasoline.

Nitro-paraffins.—A recent development in the field of nitration has been the vapor-phase low-pressure nitration of aliphatic hydrocarbons.[2] The hydrocarbon, propane for example, is vaporized and mixed with vaporized nitric acid to give at least a 2:1 ratio of hydrocarbon to acid. The reactions, nitration and oxidations take place very quickly and at around 400°C. The vapors are condensed rapidly to give layers of nitroparaffins and nitric acid, with the vapors of excess propane and the products of oxidation passing on. Various paraffins may be nitrated with similar procedures. It is characteristic of these nitrations that the original carbon chain may be reacted at any point to yield a variety of products.

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[1] *Cf.* GROGGINS, "Unit Processes in Organic Chemistry," 2d ed., p. 49, McGraw-Hill Book Company, Inc., New York, 1938; FIERZ-DAVID, "Dye Chemistry," p. 79, D. Van Nostrand Company, Inc., New York, 1921.

[2] HASS, HODGE, and VANDERBILT, Nitration of Gaseous Paraffins, *Ind. Eng. Chem.*, **28**, 339(1936); HASS and RILEY, The Nitroparaffins, *Chem. Rev.*, **32**, 373 (1943), an excellent bibliography and summary.

$$\begin{matrix}\text{Propane (in excess)}\\ + \\ \text{Nitric acid}\end{matrix} \rightarrow \left\{\begin{matrix}CH_3CH_2CH_2NO_2\\ CH_3CHNO_2CH_3\\ CH_3CH_2NO_2\\ CH_3NO_2\end{matrix}\right. + \begin{matrix}CO_2\\ H_2O\\ NO\\ \text{etc.}\end{matrix}$$

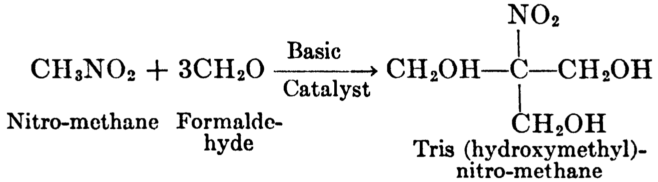
These reactions have been described,[1] and the equipment has been pictured. The material of construction is essentially stainless steel arranged in a continuous series of heaters, reactor, condensers, distillation columns with the necessary pumps, and control instruments.

The nitro-paraffins are so very reactive and offer raw materials that can be employed in so many useful syntheses that they promise to become the basis of an important branch of chemical industry. Typical syntheses from the nitro-paraffins are as follows:

1. *Reduction to Amines:*

$$\underset{\text{2-Nitro-propane}}{CH_3CHNO_2CH_3} + \underset{\text{Hydrogen}}{3H_2} \rightarrow \underset{\text{Isopropylamine}}{CH_3CHNH_2CH_3} + \underset{\text{Water}}{2H_2O}$$

2. *Addition of an Aliphatic Aldehyde:*



$$\underset{\text{Nitro-methane}}{CH_3NO_2} + \underset{\text{Formaldehyde}}{3CH_2O} \xrightarrow[\text{Catalyst}]{\text{Basic}} \underset{\text{Tris (hydroxymethyl)-nitro-methane}}{CH_2OH{-}\overset{\displaystyle NO_2}{\underset{\displaystyle CH_2OH}{C}}{-}CH_2OH}$$

3. *Addition of an Aromatic Aldehyde:*

$$\underset{\text{2-Nitro-propane}}{CH_3CHNO_2CH_3} + \underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow{\text{KOH}} \underset{\text{2-Nitro-2-methyl-1-phenyl-1-propanol}}{C_6H_5CHOHC(CH_3)NO_2CH_3}$$

4. *Formation of Hydroxylamine or Salts:*

$$\underset{\text{1-Nitro-propane}}{CH_3CH_2CH_2NO_2} + H_2SO_4 + H_2O \rightarrow \underset{\text{Hydroxylammonium acid sulfate}}{NH_2OH{\cdot}H_2SO_4} + \underset{\text{Propionic acid}}{CH_3CH_2COOH}$$

---

[1] GABRIEL, The Nitro-paraffins and Their Derivatives, *Chem. Industries*, **45**, 664 (1939); GABRIEL, The Nitro-paraffins, New Synthetics for Synthesis, *Ind. Eng. Chem.*, **32**, 887 (1940).

ESTERIFICATION

The making of esters is important for solvents, plasticizers, medicines, and perfumes. Also certain nitrate esters such as nitro-glycerine and nitro-cellulose are among the most powerful explosives (Chap. XXII). The acids used may be either organic like acetic and salicylic, or inorganic like nitric and phosphoric.

Ethyl Acetate.[1]—This is an important solvent particularly in lacquers. It is manufactured by the following reaction:

$$CH_3CH_2OH + CH_3COOH \overset{H_2SO_4}{\rightleftarrows} CH_3COOC_2H_5 + H_2O$$

Reactions such as this must be forced to completion by applying the law of mass action. In other words, one or more of the products must be removed as they are formed, and an excess of one reagent employed. Such reactions are also accelerated by using a catalyst such as sulfuric acid. The raw materials are acetic acid, ethyl alcohol in excess, and a little sulfuric acid. They are mixed, conducted through heat exchangers, and passed through an esterification column, the overhead of which is the ternary (boiling point 70.2°C.) having the composition: 82.6 per cent ethyl acetate, 8.4 per cent ethyl alcohol, and 9 per cent water. Frequently some water is added to the condensate to remove most of the alcohol which is returned to the system. The ester carrying about 4 per cent of water is rectified through a column, the water going overhead as a constant boiling mixture. It should be noted that all of the acetic acid reacts by virtue of the mass action of the excess alcohol. Ethyl acetate is consumed in such large quantities that this esterification is frequently conducted in a continuous manner. The equipment is almost invariably constructed from copper.

Other esters are manufactured in a somewhat similar manner, such as methyl salicylate, methyl anthranilate, ethyl lactate, butyl acetate, amyl acetate, diethyl phthalate, and dibutyl phthalate.

Esterification of Olefins.—Another important type of esterification is carried out by the addition of an acid to an unsaturate such as ethylene.

$$CH_2{:}CH_2 + H_2SO_4 \rightarrow C_2H_5OSO_2OH$$

The acid ester is then hydrolyzed by dilution and heat.

$$C_2H_5OSO_2OH + H_2O \rightarrow C_2H_5OH + H_2SO_4$$

This is an alternative procedure for the manufacture of ethyl alcohol in competition with the fermentation procedure described in Chap. XXXI. Propylene can be similarly reacted:

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[1] Details of various procedures and the physical chemistry involved, are presented by Groggins, *op. cit.*, pp. 548–549, 572–576.

$$CH_3{\cdot}CH{:}CH_2 + H_2SO_4 \rightarrow CH_3CH(OSO_3H)CH_3$$
$$CH_3CH(OSO_3H)CH_3 + H_2O \rightarrow CH_3CHOHCH_3 + H_2SO_4$$

The propylene from petroleum cracking-still gases is passed up through packed towers at 75 to 80°F. countercurrent to 97 per cent sulfuric acid, the acid absorbing approximately 50 per cent by weight of the propylene. The reaction mixture is taken to a lead-lined dilution tank where the concentration of isopropyl sulfuric acid is reduced to 20 per cent. Heating now hydrolyzes this ester and the isopropyl alcohol distills over. Isopropyl alcohol is used extensively as a solvent and as a rubbing alcohol, but its most important consumption is in the preparation of acetone.

$$CH_3CHOHCH_3 \rightarrow CH_3COCH_3 + H_2$$

This reaction is carried out by passing the isopropyl alcohol over a copper-gauze catalyst at 300°C. Acetone is also prepared by fermentation as presented in Chap. XXXI.

Vinyl Esters.—The addition of acids to acetylene furnishes valuable esters.

$$CH{\vdots}CH + CH_3COOH \rightarrow \underset{\text{Vinyl acetate}}{CH_3COOCH{:}CH_2} \tag{1}$$
$$CH{\vdots}CH + HCl \rightarrow \underset{\text{Vinyl chloride}}{CH_2{:}CHCl} \tag{2}$$

If two molecules of acid react, a compound such as ethylidene diacetate is formed.

$$CH{\vdots}CH + 2CH_3COOH \rightarrow (CH_3COO)_2CHCH_3 \tag{3}$$

Reactions (1) and (3) are carried out together[1] as shown in Fig. 2. Oleum, acetic acid, and mercuric oxide are mixed to give a mercury sulfate-mercury acetate catalyst. This, plus acetylene gas and acetic acid, goes into a continuous-reaction kettle which can be heated by steam. The products leave the reactor as vapors, are condensed, and led to a column still. The vapors from the top of the column, containing chiefly vinyl acetate, are condensed and sent to a rectification system to give the refined vinyl acetate, recovered acetic acid, and by-product acetaldehyde. This entire process must be carried on in an anhydrous state. The sludge coming off the bottom of the kettle goes to a settler. Here the solids are separated and returned to the mercury recovery system, while the liquids are treated in a rectification system to give the ethylidene diacetate. The reaction kettle may be constructed of Duriron. The vinyl acetate plus vinyl chloride produced according to the reactions above is consumed in the making of vinylite resins (*cf.* Chap. XXXV).

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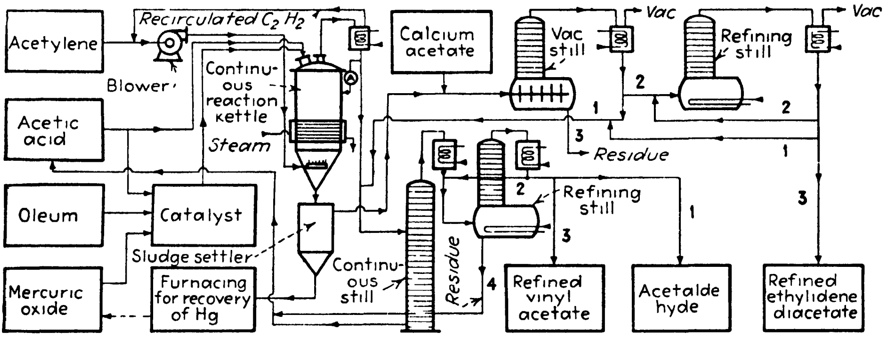
[1] ANON., Vinyl Acetate, *Chem. & Met. Eng.*, **42**, 596 (1935); MORRISON and SHAW, Vinyl Plastics from Carbide, *Chem. & Met. Eng.*, **40**, 293 (1933).

The ethylidene diacetate is distilled with sodium pyrophosphate or zinc chloride to give acetic anhydride and acetaldehyde.

$$(CH_3COO)_2CHCH_3 \rightarrow (CH_3CO)_2O + CH_3CHO$$

Miscellaneous Esters.—Cellulose acetate and cellulose xanthate are extensively manufactured for the synthetic fibers industry as described in Chap. XXXIV. An important series of compounds, the Gardinols or long-chain sodium alkyl sulfates, finds extensive use as wetting agents and detergents (*cf.* Chap. XXIX). In Fig. 1 the making of some additional esters, methyl formate for example, is shown in outline.



Numerals such as 1, 2 refer to order of cuts of still products. At Ⓐ kettle is refluxed if process is being run for production of ethylidene diacetate only, without vinyl acetate

FIG. 2.—Vinyl acetate and ethylidene diacetate.

AMINATION BY REDUCTION

These reactions are widely used for the production of dye intermediates and a more complete discussion of them may be found in Chap. XXXVIII. However, nitro-paraffins and nitriles are being reduced more extensively each year to meet the demands for amines as emulsifying agents, for absorption of gases, and for many other purposes.

AMINATION BY AMMONOLYSIS

Amination by ammonolysis[1] relates to those reactions in which an amino compound is formed using ammonia or a substituted ammonia as the agent.

Ethylenediamines.—An important application of this unit process is in the manufacture of ethylenediamine from ethylene dichloride. This latter compound is treated in a pressure autoclave with aqueous ammonia at 100 to 180°C.

$$CH_2ClCH_2Cl + 4NH_3 \rightarrow CH_2NH_2CH_2NH_2 + 2NH_4Cl$$

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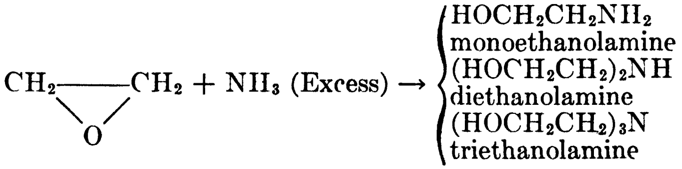
[1] GROGGINS, *op. cit.*, Chap. 6, pp. 299–361.

A large excess of ammonia is used in order to favor the formation of the primary amine over the various secondary products: even then only a 40 per cent yield of the desired product is obtained. It is used as a corrosion inhibitor, a solvent for vat dyes, a latex stabilizer and its fatty acid derivatives are employed as detergent

Ethanolamines.—A mixture of mono-, di- and triethanolamines is obtained when ethylene oxide is bubbled through 28 per cent aqueous ammonia at 50 to 60°C. as shown by the following equations:



These compounds, usually sold as a mixture, find extensive use in cosmetics as emulsifying agents and as ingredients for dry-cleaning soaps.

Methylamines.—Ammonia under pressure may be used to replace an —OH group as well as a halogen atom. An example of this is the preparation of methylamines from methanol. This reaction is carried out in the vapor phase by passing a mixture of methanol and ammonia in the ratio of 1:5 over an alumina gel catalyst held at 450°C. The pressure is 200 lb. per sq. in. About 13.5 per cent monomethylamine, CH_3NH_2; 7.5 per cent dimethylamine, $(CH_3)_2NH$; and 10.5 per cent trimethylamine, $(CH_3)_3N$, are obtained on the basis of the ammonia. The recirculation of monoamine raises the yield of the diamine.

Hexamethylenediamine.—This is a striking example of a chemical that is now in large-scale production where only a few years ago it was a laboratory curiosity. It is prepared by a two-step amination of adipic acid. The adipic acid is first treated with ammonia and a dehydrating catalyst at 320 to 400°C. in the vapor phase to produce adiponitrile.

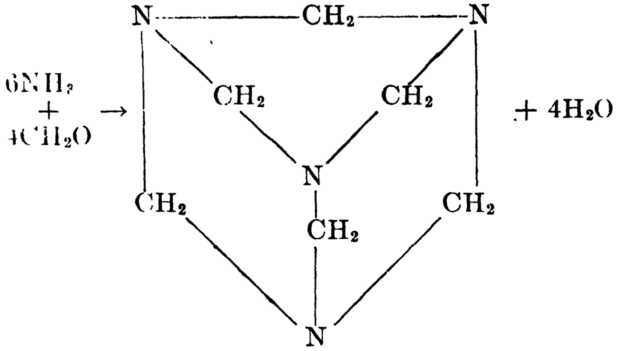
$$HO_2C(CH_2)_4CO_2H + 2NH_3 \rightarrow NC(CH_2)_4CN + 4H_2O$$

The adiponitrile is reacted with hydrogen in the presence of ammonia in the liquid phase under pressure below 200°C. to produce hexamethylenediamine (1,6-hexanediamine).

$$NC(CH_2)_4CN + NH_3 + 4H_2 \rightarrow H_2N(CH_2)_6NH_2 + NH_3$$

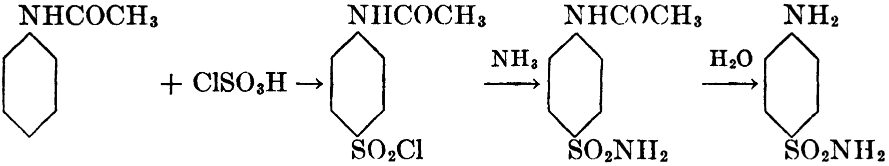
This compound finds extensive consumption in the making of Nylon (Chap. XXXIV).

Hexamethylenetetramine.—Evaporation of the reaction product of formaldehyde and ammonia produces hexamethylenetetramine. This compound finds use as a



urinary antiseptic (Urotropine), in the rubber industry, and in the preparation of the explosive, cyclonite (Chap. XXII). It is also consumed in the making of phenol-formaldehyde resins where it is known as *hexa.*

Sulfanilamide.—This new and increasingly important compound is manufactured by the following series of reactions:



Sulfanilamide is used widely as a specific cure for infections caused by streptococcus and some other organisms. Many similar compounds have also been prepared that possess excellent bactericidal properties. Of these the more important are sulfapyridine, sulfathiazole, and sulfadiazine.[1]

HALOGENATION

Halogenation is the process of introducing halogen atoms into an organic molecule. This may be carried out by substitution for hydrogen, addition to an unsaturated bond, or replacement for an —OH or a —SO_3H group.

Chlorination of Aliphatics.—The direct chlorination of aliphatic hydrocarbons has been studied by Hass[2] and coworkers at Purdue University. The various products are obtained through both liquid- and vapor-phase reactions, using various temperatures and pressures, and with or without catalysts. The mixtures of products are separated by rectification. These chloro-aliphatics find many uses commercially; for example, for the production of amyl alcohols from chloro-pentanes and as solvents, particularly in dry cleaning under nonflammable conditions.

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[1] FURNAS, editor, "Rogers' Manual of Industrial Chemistry," 6th ed., D. Van Nostrand Company, Inc., New York 1942. See Chap. 34 by Shonle, particularly p. 1312.

[2] HASS, *et al.*, Syntheses from Natural Gas Hydrocarbons, *Ind. Eng. Chem.*, **23**, 352 (1931); HASS, MCBEE, and WEBER, *Ind. Eng. Chem.*, **28**, 333 (1936); HASS and WEBER, *Ind. Eng. Chem.*, *Anal. Ed.*, **7**, 231 (1935); HASS, MCBEE, and HATCH, *Ind. Eng. Chem.*, **29**, 1335 (1937).

Benzyl Chloride.—To produce benzyl chloride, toluene and chlorine are reacted under conditions different from those employed for the ring chlorination yielding chloro-benzene as described in Chap. XXXVIII. This reaction is carried out in the *absence* of iron, the temperature being at

$$C_6H_5CH_3 + Cl_2 \rightarrow C_6H_5CH_2Cl + HCl$$

130 to 140°C. and with the reaction mixture circulating through a glass arm in the autoclave where *light catalyzes* the reaction. This product is used in making benzyl alcohol and other chemicals incorporated in perfumes as well as benzyl derivatives.

Ethylene Dichloride.—The addition of halogen to unsaturates serves to give many valuable derivatives such as ethylene dichloride, ethylene dibromide, dichloro-ethylene, trichloro-ethylene, and tetrachloro-ethane. The preparation of ethylene dichloride is a typical example.

$$CH_2{:}CH_2 + Cl_2 \xrightarrow{C_2H_4Br} ClCH_2CH_2Cl$$

The chlorine gas is bubbled through a tank of ethylene dibromide and the mixed vapors sent to a chlorinating tower where they meet a stream of ethylene. Here reaction takes place at a temperature of 40 to 50°C. The products from the tower pass through a partial condenser followed by a separator, the crude ethylene dichloride passing off as a gas and the liquid ethylene dibromide being returned to the process. The product enters into further synthesis as in the preparation of ethylenediamine and Thiokol. It is also used as a solvent.

Ethylene Dibromide.—This compound, commonly known as *ethylene bromide,* is prepared by the direct addition of bromine to ethylene. It is used in very large quantities as an additive reagent to tetraethyl lead in gasoline. It serves to prevent the deposition of lead oxide on the valves of the gasoline engine.

Carbon Tetrachloride.[1]—A typical example of a replacement reaction is found in the preparation of carbon tetrachloride. Carbon disulfide is treated with chlorine in the presence of iron in a lead-lined still with a reflux condenser and heating coils.

$$CS_2 + 3Cl_2 \xrightarrow{Fe} S_2Cl_2 + CCl_4$$

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[1] FURNAS, *op. cit.,* p. 467.

These products are separated by distillation and the sulfur monochloride is treated with CS_2 to give more carbon tetrachloride.

$$CS_2 + 2S_2Cl_2 \rightarrow CCl_4 + 6S$$

When the reaction mixture from the latter step is cooled, the sulfur precipitates, and the carbon tetrachloride is separated and further purified by rectification. The sulfur is converted back to carbon disulfide. The solvent properties of carbon tetrachloride direct its use as a degreasing agent and dry-cleaning fluid. It is also employed in fire extinguishers.

Ethyl Chloride.—Halogen acids also may be used to give halogenated derivatives. HCl reacts with ethylene both being in the liquid phase, in the presence of a catalyst such as aluminum chloride, to give ethyl chloride.

$$CH_2{:}CH_2 + HCl \xrightarrow{AlCl_3} CH_3CH_2Cl$$

Such a reaction may be carried out as a batch process by bringing the reagents together in a pressure vessel. A low temperature is used. HCl may also be made to react with ethyl alcohol to give ethyl chloride according to the equation:

$$CH_3CH_2OH + HCl \rightarrow CH_3CH_2Cl + H_2O$$

This reaction will probably not compete with cheap ethylene from petroleum cracking. The use of ethyl chloride in the making of tetraethyl lead is its most important consumption. It is also employed as a refrigerant, solvent, and anesthetic.

Ethylene Chlorohydrin.—Hypohalogen acids also add to unsaturates, ethylene chlorohydrin being made according to the equations:

$$CaO + H_2O + 2Cl_2 \rightarrow CaCl_2 + 2HOCl$$
$$HOCl + CH_2{:}CH_2 \rightarrow CH_2OHCH_2Cl$$

In commercial operation, a hydrated lime suspension is passed down a tower countercurrent to a stream of ethylene at 200 atm. and 20°C., thus giving a solution of ethylene in lime water. Chlorine is introduced and the reactants are passed to a chamber where the hypochlorous acid reacts with the ethylene. The ethylene chlorohydrin-calcium chloride solution coming from the reactor may be treated to give ethylene glycol (page 916). This latter is highly valued as an antifreeze.

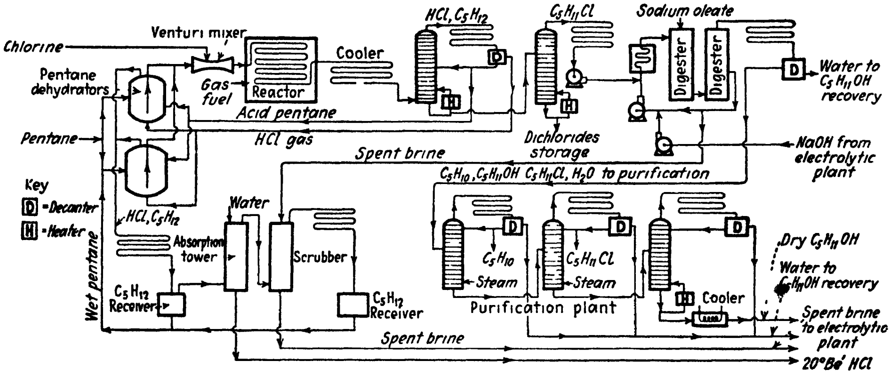
SULFONATION

Since the sulfonation unit process is applied principally to intermediates and dyes, see Chap. XXXVIII for description and examples. At present, certain detergents employ sulfonation in building up their molecules though usually sulfate esterification is the chosen process.

HYDROLYSIS

Hydrolysis,[1] as the name implies, involves the reaction of water, usually in a double decomposition. In almost every case, an accelerating agent is necessary to carry out the process commercially. The hydrolysis. of starch to dextrose is presented in Chap. XXX, of fats to soaps in Chap. XXIX, of sulfonates and halides to hydroxy derivatives in Chap. XXXVIII, and of ethyl alcohol from ethylene under esterification in this chapter.

Amyl Alcohols.—The manufacture of amyl alcohols from the chloropentanes[2] is a typical hydrolysis reaction and is shown in Fig. 3 together with the preceding chlorination. *n*-Pentane and isopentane are separated from natural gasoline and chlorinated in the vapor phase at 250 to 300°C. The products pass through a heat exchanger to the rectification unit where the hydrogen chloride and the dichlorides (5 per cent) are removed. The hydrolysis of the monochlorides is carried out in a system of digesters, pumps, and heaters through which a hot emulsion of amyl alcohol, water, and sodium oleate circulates. The amyl chlorides and sodium hydroxide solution are continuously added to the system, and a spent brine and crude amyl alcohol vapors are continuously withdrawn. The salt solution is scrubbed to remove alcohol vapors and then returns to the electrolytic cells where the necessary chlorine and caustic for the process are



Main reactions $C_5H_{12} + Cl_2 \longrightarrow C_3H_{11}Cl + HCl$
$C_5H_{11}Cl + NaOH \longrightarrow C_5H_{11}OH + NaCl$

Side reactions $C_5H_{12} + 2Cl_2 \longrightarrow C_5H_{10}Cl_2 + 2HCl$
$C_5H_{11}Cl \longrightarrow C_5H_{10} + HCl$
$C_5H_{10} + Cl_2 \longrightarrow C_5H_{10}Cl_2$

Reacting quantities not known, weight of 100% HCl produced approx 50% of chlorine charged

FIG. 3.—Flow chart for production of amyl alcohols (Pentasol) from pentanes—Sharples procedures.

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[1] LLOYD and PALMER in Chap. 11 of Groggins, *op. cit.*, discuss the various aspects of this unit process.

[2] ANON., Synthetic Amyl Alcohol and Acetate, *Chem. & Met. Eng.*, **47**, 493 (1940), pictured flow sheet.

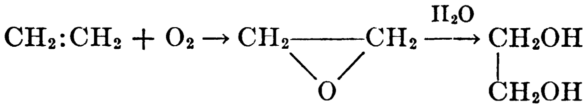
made. The crude amyl alcohol vapors are condensed and rectified to give the following products as shown in Fig. 3: (1) amylene which is hydrated to amyl alcohol, (2) unchanged amyl chlorides to be returned to process, (3) diamyl ether, (4) special amyl alcohol fractions, (5) the mixture of amyl alcohols sold under the name Pentasol and used as lacquer solvents.

Ethylene Glycol.—The important permanent antifreeze, ethylene glycol, is made by several processes, involving hydrolysis. In the first, ethylene chlorohydrin is treated with sodium bicarbonate solution.

$$CH_2OHCH_2Cl + NaHCO_3 \rightarrow CH_2OHCH_2OH + NaCl + CO_2$$

The chlorohydrin solution is concentrated to 35 to 40 per cent and reacted with the theoretical amount of sodium bicarbonate solution in a closed, stirred, steam-jacketed kettle. At a temperature of 70 to 80°C., the hydrolysis proceeds smoothly with the evolution of CO_2 and is complete in 4 to 6 hr. The glycol solution is concentrated by distillation. As the high-boiling ethylene glycol can be separated only with difficulty from the salt, it is presumably better engineering to make ethylene oxide out of the ethylene chlorohydrin by heating with caustic soda or hydrated lime. This would then be hydrated to the glycol by treating with weakly acidulated water under low pressure.

Another method for making glycol is by the reaction of ethylene, oxygen, and water in the presence of a silver catalyst. The reaction is probably stepwise, involving oxidation and subsequent hydrolysis.



$$CH_2{:}CH_2 + O_2 \rightarrow \underbrace{CH_2\text{——}CH_2}_{O} \xrightarrow{H_2O} \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$$

A recent high-pressure process for ethylene glycol involves the following reactions:

$$CH_2O + CO + H_2O \rightarrow CH_2OH{\cdot}COOH$$
$$CH_2OH{\cdot}COOH + 2H_2 \rightarrow CH_2OH{\cdot}CH_2OH + H_2O$$

Gallic Acid.—Gallic acid, 3,4,5-trihydroxybenzoic acid, is obtained by the hydrolysis of the glucoside, tannic acid, found in nutgalls and sumac. The process consists of an alkaline or acid autoclaving of the water extracts of the nutgalls. It may also be prepared by fermentation of an extract with *Aspergillus niger* or *Aspergillus gallomyces*. The gallic acid is purified by several recrystallizations from water using nonferrous equipment. The chief uses of gallic acid are in the manufacture of dyes and as a raw material for the production of pyrogallol and bismuth subgallate. It is also a constituent of many inks where the ferric gallate formed on oxidation is the permanent pigment.

OXIDATION

Oxidation is one of the most valuable tools to the synthetic chemist. The possibilities of this process are so varied that a type reaction is impossible. However, it may be said that it involves the addition of oxygen to a molecule or the removal of hydrogen from it. The cheapest reagent, and the one always employed when possible, is air. The reactions are carried out in both the liquid and vapor phases, using a variety of catalysts, V_2O_5 for example. In the latter case, fairly high temperatures (about 400°C.) are employed and, since the reactions are highly exothermic, the problem of heat removal is a large one. This is described under Phthalic Anhydride in Chap. XXXVIII, page 859.

Camphor.—An organic chemical produced by oxidation is camphor. The raw material for this process is turpentine and the following steps are involved: (1) distillation of turpentine to obtain pinene, (2) saturation with HCl gas giving bornyl chloride, (3) hydrolyzing this to obtain camphene, (4) esterifying to give isoborneol acetate, (5) saponification to isoborneol, and (6) oxidation to camphor. The last reaction is carried out in the liquid phase using nitric acid as the reagent. Twenty parts of isoborneol are dissolved in 100 parts of 1.32 sp. gr. nitric acid plus 5 parts of 50 per cent sulfuric acid. The mixture is heated to 80 to 90°C. and stirred well for 10 hr. The largest use of camphor is as a plasticizer in various resins. It is also consumed in many pharmaceutical preparations.[1]

Formaldehyde.—The oxidation of methanol to formaldehyde is an important commercial process.

$$CH_3OH + \tfrac{1}{2}O_2 \xrightarrow{Ag} H_2CO + H_2O \text{ (Exothermic)}$$

The oxidation requires 26.7 cu. ft. of air per pound of methanol reacted, a ratio that is maintained by passing separate streams of these two materials into a vaporizing chamber. These vapors pass to a catalyst chamber consisting of 24-in. copper tubes, 2 in. in diameter, containing rolled-up silver or copper gauze. Here the oxidation occurs at a temperature of 550 to 600°C., the product being recovered in solution by a rectifying and scrubbing system. The yield in the reaction is 85 per cent, the formaldehyde being marketed as a 37 per cent solution sometimes called Formalin.[2] Much of the equipment is made of stainless steel. Formaldehyde is competitively manufactured by controlled oxidation of natural gas or methane.[3]

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[1] GUBELMANN and ELLEY, Production of Synthetic Camphor from Turpentine, *Ind. Eng. Chem.*, **26**, 589 (1934); GROGGINS, *op. cit.*, p. 378.

[2] HOMER, Formaldehyde, Properties, Analysis and Manufacture, *J. Soc. Chem. Ind.*, **60**, 213 (1941).

[3] ANON., Formaldehyde from Natural Gas, *Chem. & Met. Eng.*, **49**, No. 9, 154 (1942), pictured flow sheet.

Acetic Acid.—Various methods for the manufacture of acetic acid involve oxidation. Thus, the production from acetylene goes through the following reactions:

$$C_2H_2 + H_2O \rightarrow CH_3CHO \qquad (1)$$
$$CH_3CHO + \tfrac{1}{2}O_2 \rightarrow CH_3COOH \qquad (2)$$

Reaction (1) is carried out by passing acetylene into a suspension of mercurous sulfate in 25 per cent sulfuric acid in a Duriron kettle under a pressure of 15 lb. per sq. in., as shown in Fig. 4. The temperature is maintained between 70 and 100°C. by the heat of reaction. As a result of side reactions the catalyst is reduced to metallic mercury, necessitating the addition of make-up catalyst every 15 min. and complete change every 8 hr. A series of scrubbers and condensers removes the acetaldehyde from the effluent gases, the yield being 95 per cent. The oxidation of acetaldehyde is carried out in a series of two aluminum-lined steel vessels. Here, at a temperature of 55°C. and a pressure of 70 lb. per sq. in., air is used to carry out the reaction, 0.1 per cent of manganese acetate being used to hold down the concentrations of the explosive intermediate, peracetic acid. The crude acetic acid of 94 per cent strength is taken off from the second reactor and rectified.

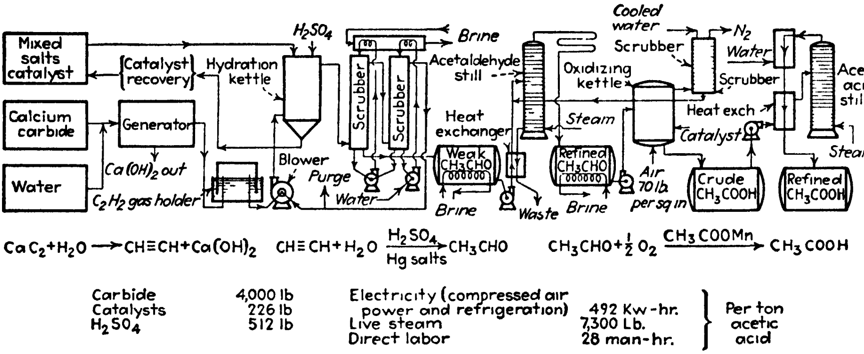


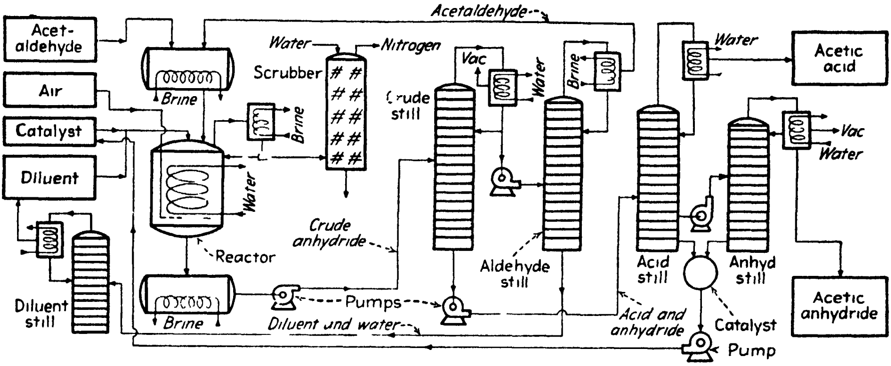
FIG. 4.—Flow chart for acetic acid from carbide.

Acetaldehyde for oxidation is also made from ethyl alcohol according to the following reactions which occur simultaneously:

$$C_2H_5OH + \tfrac{1}{2}O \rightarrow CH_3CHO + H_2O$$
$$C_2H_5OH \rightarrow CH_3CHO + H_2$$

The reaction is exothermic taking place at 550 to 570°C. upon passing through a silver-gauze catalyst with the alcohol vapors entering at 160°C. and the air at 200°C. The yield is 85 to 95 per cent, the conversion 50 to 55 per cent, and the product is recovered by scrubbing the vapors from the reactor with ethyl alcohol and then rectifying to give 99 per cent acetaldehyde. Acetic acid is also made from CH_3OH and CO as shown in Fig. 1.

Acetic Anhydride.—Acetaldehyde, produced by either of the methods discussed above under Acetic Acid, may be oxidized to acetic anhydride according to the process shown in Fig. 5. The acetaldehyde is oxidized by air in the main reactor with methyl acetate diluent and with manganese acetate catalyst present to prevent the formation of explosive amounts of peracetic acid.[1] The pressure is around 60 lb. per sq. in. and the temperature at 50 to 70°C. The products, acetic anhydride and acetic acid, are purified in a series of bubble-cap columns, with the crude still and the anhydride still operating under vacuum. The most important use of acetic anhydride is in the making of cellulose acetate. It is also employed in various other acetylations.



Main Reactions
$CH_3CHO + O_2 \rightarrow CH_3COOOH$ (peracetic acid)
$CH_3COOOH + CH_3CHO \rightarrow H_2O + (CH_3CO)_2O$ (acetic anhydride)
$(CH_3CO)_2O + H_2O \rightarrow 2\ CH_3COOH$ (acetic acid)

FIG. 5.—Flow chart for acetic anhydride from acetaldehyde.

Adipic Acid.—Vigorous oxidation of cyclohexanol (prepared by hydrogenating phenol) produces adipic acid, $HO_2C(CH_2)_4CO_2H$. This compound is extensively used in the preparation of Nylon in combination with hexamethylenediamine.

HYDROGENATION

Hydrogenation is employed in the chemical industries today to give many useful products. The various methods for the production of hydrogen are discussed fully in Chap. VIII. Besides the addition of hydrogen to double bonds, this reaction may be used to eliminate other elements from a molecule, as is done in petroleum hydrogenations. These include mainly oxygen, nitrogen, sulfur, carbon, and halogens. Hydrogenation is carried on under pressure and usually at elevated temperatures with a suitable catalyst. The temperatures are ordinarily below 400°C. but may extend up to 500°C. in some cases. The catalysts vary with temperature, the noble metals such as platinum or palladium being used up to 150°C., nickel and copper from 150 to 250°C., and various combinations of metals and metal oxides for the higher temperatures. Pressure not only increases the rate of reaction but, in the cases where there is a decrease in volume as the reaction proceeds, causes a desirable shift in the equilibrium according to Le Châtelier's principle. The equipment generally used consists either of a pressure autoclave or a tubular pressure system, built to withstand pressures up to 3,000 lb. per sq. in. or more. Since most hydrogenations are exothermic, the equipment should be designed to facilitate the removal of heat, especially from the catalyst chamber.

---

[1] BENSON, New Acetic Anhydride Process, *Chem. & Met. Eng.*, **47**, **150** **(1940)**.

Hydrogenation of Fatty Oils.—Some of the most familiar hydrogenated products in use today are the solid cooking fats made from various oils. This procedure is fully presented in Chap. XXVIII.

Hydrogenation of Petroleum.—The hydrogenation of petroleum is one of the most useful reactions employed in the refinery today. It serves to up-grade heavy oils and residues giving increased yields of gasoline, to produce higher octane gasoline, and to furnish improved lubricating oils. A discussion of this process is given in Chap. XXXVII.

Hydrogenation of Coal.—The hydrogenation of coal[1] to give a motor fuel is used extensively in Germany and England today but is not yet economical in this country, owing to the present low price of gasoline. The hydrogenation is carried out on a coal paste made by mixing heavy oil with finely ground soft coals. This paste is mixed with a nickel catalyst and, after preheating, is sent to the reaction chambers. Here a stream of hydrogen carries out the reaction at a temperature of 450°C., both hydrogenation and pyrolysis of the molecules taking place. The liquid product is fractionated to furnish (1) gasoline, (2) a light oil which is cracked to give more gasoline, and (3) a heavy oil which is returned to the process to make a paste with the coal. There will come a time when our coal resources will be employed to produce motor fuels by this process.

Methanol Synthesis.—One of the most important of the high-pressure syntheses in use today is the production of methanol and various higher alcohols from carbon monoxide and hydrogen.[2] The essential reaction is

$$CO + 2H_2 \rightarrow CH_3OH; \qquad \Delta H = -24{,}620 \text{ cal.}$$

The catalyst most commonly employed is copper mixed with oxides of zinc, chromium, manganese, or aluminum. For the synthesis of methanol, contact of the gases with hot iron must be avoided and so copper-lined reactors are used. The theoretical proportions of the gases are mixed and compressed to 4,500 lb. per sq. in. After oil purification, the gases go to the reactors where, at 300°C., the equilibrium yield is better than 60 per cent. The gaseous products then pass through the heat exchangers to high-pressure condensers where the methanol is condensed at 3,500 to 4,000 lb. per sq. in. with the gases being sent back to the process. Very pure (99 per cent) methanol is furnished by this process. The higher alcohols are produced at higher temperatures, 350 to 475°C., using a catalyst containing alkali (see Fig. 1).

---

[1] STORCH, Hydrogenation of Coal, *Ind. Eng. Chem.*, **36**, 291 (1944).

[2] For a discussion of high-pressure technique, see Perry, *op. cit.*, pp. 2167–2192.

Methanol finds a wide variety of direct industrial uses such as a denaturant, antifreeze, fuel, and solvent. In addition, it is the starting material in such reactions as the preparation of methylamines, formaldehyde, and dimethyl-aniline.

High-molecular-weight Aliphatic Amines.[1]—These compounds are made by catalytically hydrogenating the corresponding nitriles prepared by dehydration at elevated temperatures of the ammonium salts of the fatty acids.

$$RCO_2NH_4 \rightarrow RCONH_2 \rightarrow RCN \xrightarrow{H_2} RCH_2NH_2$$

These are essentially new industrial compounds of the "cationic" active class and are finding employment as flotation agents, in water treatment, and in textile finishing. They also possess bactericidal properties, and some of them are insecticides or insect repellents. These are commercially available with the alkyl chain in the above reaction having from 6 to 18 carbon atoms, some being shipped in carload lots.

ALKYLATION

A wide variety of reactions[2] may be employed to introduce an alkyl radical into the various organic compounds such as are classified under Alkylation in Chap. II and exemplified here and in Chap. XXXVIII.

Ethyl Ether.—Ethyl ether and other aliphatic ethers are made by the dehydrating action of sulfuric acid on an alcohol.[3]

$$C_2H_5OH + H_2SO_4 \rightarrow C_2H_5 \cdot HSO_4 + H_2O \quad (1)$$
$$C_2H_5OH + C_2H_5 \cdot HSO_4 \rightarrow C_2H_5OC_2H_5 + H_2SO_4 \quad (2)$$

The alcohol and sulfuric acid are heated to 140°C. in a lead-lined vessel. After the reaction is started, the process is continuous. A mixture of ether, alcohol, and water is constantly vaporized and rectified to furnish a pure product. The yield for the reaction is 94 per cent. Ethyl ether is also produced in the hydration of ethylene to ethyl alcohol. The first step in the process gives ethyl sulfate as above from which the second reaction proceeds. The uses of ethyl ether are many and varied. Some important ones are as a solvent, an anesthetic, and for further synthesis of organic compounds.

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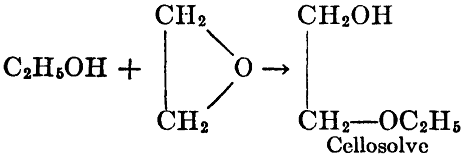
[1] RALSTON, Chemicals from Fats, *Chem. Eng. News*, **21,** 3 (1943).

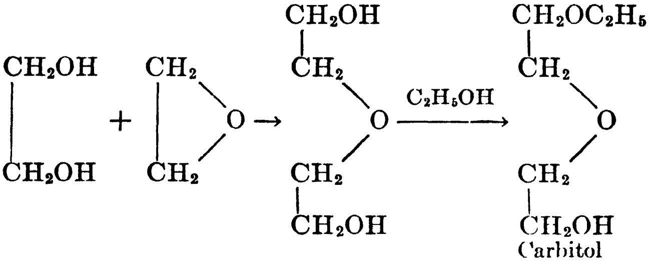
[2] See Chap. 9 on Alkylation by Shreve in Groggins, *op. cit.*

[3] BROOKS, Manufacture of Alcohols and Ethers, *Ind. Eng. Chem.*, **27,** 283 (1935).

Glycol Ethers.—A very practical series of ethers is obtained by the use of ethylene oxide as an alkylating agent. Two of these, ethylene glycol ethyl ether (Cellosolve) and diethylene glycol ethyl ether (Carbitol), are obtained by the reaction of ethylene oxide with ethyl alcohol.



(1)



(2)

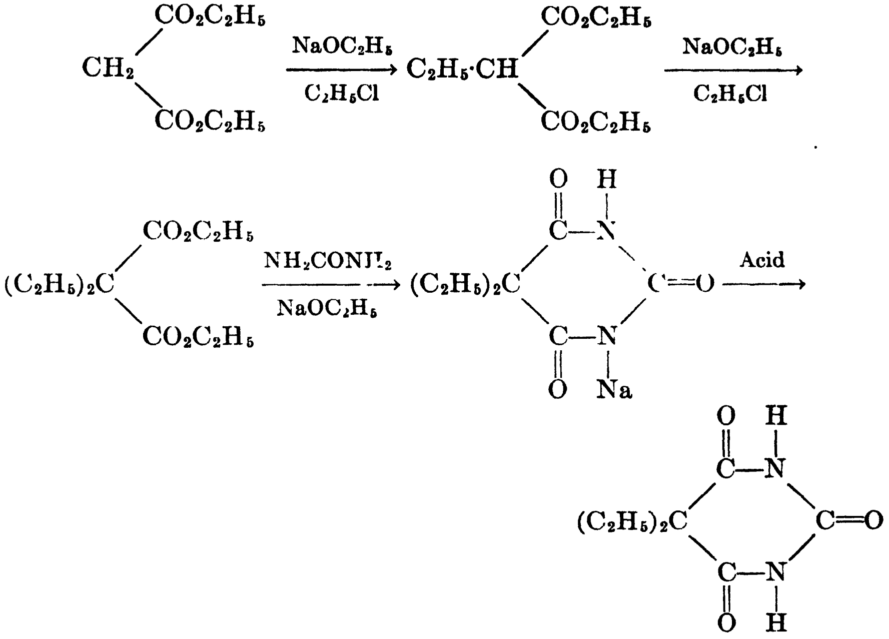
Isomers are made by varying the reactants from those given. Absolute ethyl alcohol and liquid ethylene oxide under pressure are introduced into an autoclave, the alcohol being present in 15 per cent excess. The autoclave is heated at 150°C. for 12 hr., the pressure changing from 250 lb. per sq. in. at the start, to 125 at the end. The reaction mass is fractionated, and the Cellosolve is taken off at 134°C. It is obtained in yields of 70 per cent based on the alcohol. Further distillation of the residue gives the Carbitol which boils at 201.9°C. The latter results from any ethylene glycol present in the reagents or formed by action of ethylene oxide on any water present or made. Carbitol is also manufactured directly. Both of these substances find widespread usage as specialized solvents in textiles, cosmetics, dyeing, and in sealing Cellophane packages.

Tetraethyl Lead.—A very important alkylated product is tetraethyl lead, the universal antiknock compound for gasolines. It is prepared commercially by the action of ethyl chloride on a lead-sodium alloy.

$$4PbNa + 4C_2H_5Cl \rightarrow Pb(C_2H_5)_4 + 3Pb + 4NaCl$$

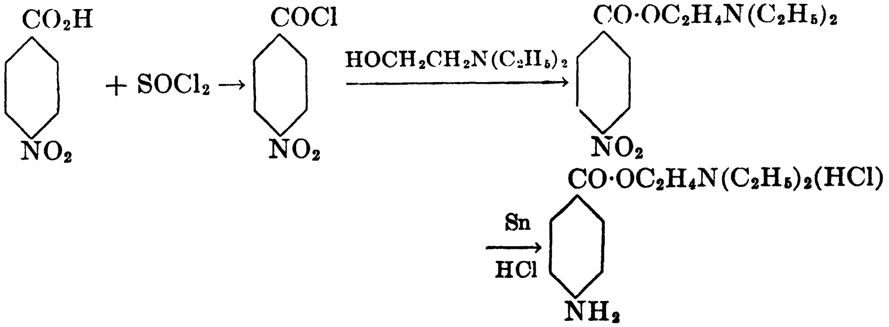
The autoclave for the reaction must have a heating jacket, a heavy-duty stirrer to agitate the lead alloy, and a reflux condenser. The alloy should be finely divided, and the temperature should be below 70°C. The reaction is heated at the start and then must be cooled to maintain the temperature at 40 to 60°C. After 2 to 6 hr., the excess ethyl chloride is distilled off and then the tetraethyl lead steam distilled from the reaction mixture.

Barbital.—Barbital (diethyl-barbituric acid) is prepared by a series of reactions starting with the ethyl ester of malonic acid.



A whole series of similar compounds may be prepared in a like manner by using alkylating agents other than ethyl chloride. For example, phenyl-ethyl-barbituric acid is known as *phenobarbital.* These compounds find extensive pharmaceutical use as hypnotics and soporifics.

Procaine (Novocaine).—The production of the important local anesthetic, procaine, involves not only the unit process of alkylation but also halogenation and reduction.

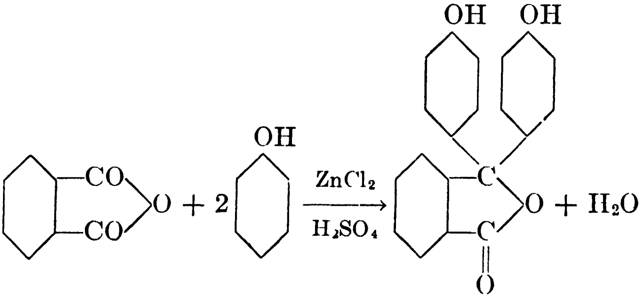


The hydroxy tertiary amine that is used to condense with the *p*-nitrobenzoyl chloride is prepared by treating ethylene chlorohydrin with diethylamine.

CONDENSATION

The unit process of condensation involves the commercial reacting of two chemicals to form a main product with the simultaneous splitting off of water, hydrogen chloride, or another simple compound.

Phenolphthalein.[1]—This compound is widely used as an acid-base indicator and also as a laxative. It is prepared by condensing phthalic anhydride with phenol in the presence of sulfuric acid.



MISCELLANEOUS UNIT PROCESSES

Formic Acid.—Two very useful acids, formic and oxalic, are produced starting with sodium hydroxide solution and carbon monoxide. Sodium hydroxide (97 to 98 per cent) is reacted with the carbon monoxide at 200°C. and under a pressure of 8 to 10 atm. in a jacketed autoclave

$$CO + NaOH \rightarrow HCOONa$$

The carbon monoxide is usually produced by the incomplete combustion of coke, followed by removal of CO_2 with an amine solvent, or by scrubbing with caustic soda. After the reaction is complete, the solution is acidified and the formic acid distilled off. The product is 90 per cent formic acid and the yield is 95 per cent. Formic acid serves for the preparation of formate esters and oxalic acid. In the anhydrous state it is employed as a solvent for certain reactions and as a reducing agent (see Fig. 1) for conversion of methanol and carbon monoxide into methyl formate and then into formic acid.

Oxalic Acid.—If, after the sodium formate is made according to the foregoing equation, the pressure is reduced in the autoclave and the temperature is raised to 375°C., sodium oxalate will be formed.

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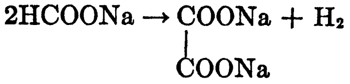
[1] ROWE, "Colour Index and Supplement," Society of Dyers and Colourists, Bradford, Yorkshire, 1924; GROGGINS, *op. cit.*, p. 648.



$$\mathrm{2HCOONa} \rightarrow \begin{array}{l}\mathrm{COONa}\\ |\\ \mathrm{COONa}\end{array} + \mathrm{H_2}$$

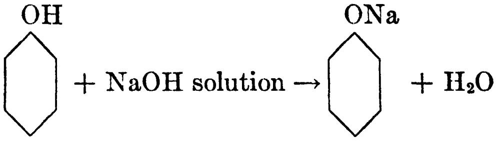
The hydrogen is exhausted from the autoclave, and the reaction is complete when no more hydrogen is evolved. Milk of lime is added to the solution and the mixture thoroughly agitated. The calcium oxalate formed is filtered off and the caustic solution is concentrated and reused.

$$Na_2C_2O_4 + Ca(OH)_2 \rightarrow CaC_2O_4 + 2NaOH$$

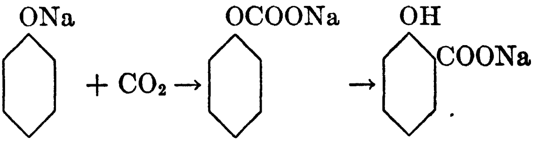
The calcium oxalate, plus some calcium carbonate that is present, is reacted with dilute sulfuric acid. Much of the calcium precipitates as $CaSO_4 \cdot 2H_2O$ while on concentration the remaining calcium sulfate present precipitates out and is filtered off. Further concentration to 30°Bé., followed by cooling, causes the oxalic acid to crystallize. These crystals are removed and washed in a centrifuge while the mother liquor is employed for make-up in subsequent runs.

The uses of oxalic acid are many and varied. Some of the important ones are as a germicide, a bleaching agent, a solvent, and as a starting material in the manufacture of various other chemicals, especially many simple and complex oxalates.

Salicylic Acid.—Salicylic acid[1] is made by the Kolbe reaction from CO_2 (see Fig. 6). The starting material is phenol, which is run into hot aqueous caustic soda to give sodium phenate. This step is carried out in a heated iron tank.



The resulting solution is evaporated to dryness in stirred autoclaves under vacuum at 130°C. The sodium phenate must be absolutely dry; to ensure this, certain manufacturers conduct this unit operation in a heated ball mill so that the material being dried is simultaneously ground up. The temperature is reduced to 100°C., and dry CO_2 gas is introduced under 6 atm. pressure. The following reactions occur:



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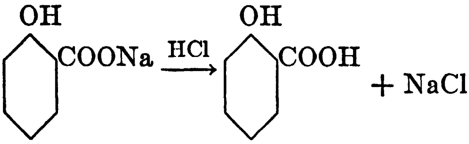
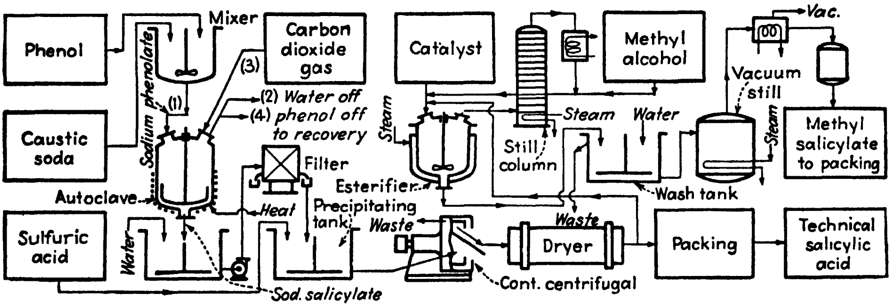
[1] SHONLE, p. 1305, in Furnas, *op. cit.;* pictured flow sheet in *Chem. & Met. Eng.*, **50**, No. 8, 132–135 (1943).

The sodium salicylate is dissolved in water and decolorized by passing through activated carbon containing some Zn powder. The solution is acidified with excess hydrochloric acid, precipitating the salicylic acid.



Salicylic acid is used as a medicinal and an intermediate in the production of other medicinals, but the largest consumption is in the making of aspirin, acetyl salicylic acid. It also finds use as an antiseptic.



Reactions: $2C_6H_5OH + 2NaOH \rightarrow 2C_6H_5ONa + 2H_2O$

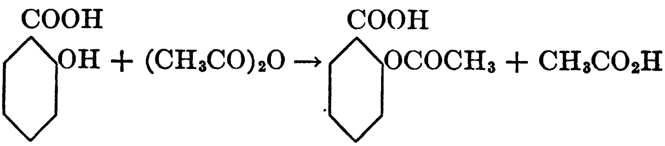
$2C_6H_5ONa + CO_2 \rightarrow ONaC_6H_4COONa + C_6H_5OH$

$ONaC_6H_4COONa + H_2SO_4 \rightarrow OHC_6H_4COOH + Na_2SO_4$

$OHC_6H_4COOH + CH_3OH \rightarrow OHC_6H_4COOCH_3 + H_2O$

FIG. 6.—Flow sheet for salicylic acid and methyl salicylate.

Aspirin.—Aspirin, acetyl salicylic acid, is prepared by acylating salicylic acid with acetic anhydride. It is widely used as a pain-relieving drug.



Tartaric Acid.—Tartaric acid,[1] dihydroxysuccinic acid, has the formula:

$$HOOCCHOHCHOHCOOH$$

---

[1] ULLMANN, "Enzyklopaedie der technischen Chemie," 2d ed., Vol. 10, p. 471, Urban & Schwarzenberg, Berlin and Vienna, 1928–1932.

This occurs as its dextro-rotary isomer and as its crude acid potassium salt with some calcium salt in argols and wine lees—the solid deposits left in a wine vat after fermentation. The pure acid potassium salt, $KHC_4H_4O_6$, cream of tartar, is obtained by leaching with water, precipitation of the calcium and other impurities, evaporation, and crystallization, followed by recrystallization if necessary. It is dried and powdered for use as an ingredient of baking powders.

Tannic Acid.—Tannic acid, a glucoside of gallic acid, is obtained by countercurrent extraction of nutgalls by water. The extract as obtained is 10 to 11°Bé. The equipment is constructed either of copper or of wood. It is imperative that no iron be present as iron reacts with tannic acid to form black iron tannate. Even traces of iron are sufficient to discolor the product. The water extract is concentrated in volume and, on drying, yields technical tannin which is used as a mordant in dyeing and as a source of gallic acid. Extraction of nutgalls with alcohol or ether, bleaching of the extract with mild reducing agents, such as sodium bisulfite, and evaporation of the extract yield medicinal grade tannin. This is used for burns, as an astringent, in gargles, and to precipitate proteins in wineries and breweries.

Pyrogallol.—Pyrogallol, 1,2,3-trihydroxybenzene, is obtained by decarboxylating gallic acid. The gallic acid is autoclaved with water at 12 atm. and 200°C. with copper equipment. The reaction is complete when no more carbon dioxide is evolved, and the water solution is then evaporated to dryness. The solid pyrogallol is purified by sublimation[1] *in vacuo* or in superheated carbon dioxide. It is used in photography, for dyeing, medicinally to treat skin diseases, and as an oxygen absorbent in analytical chemistry.

Alkaloids.—Alkaloids[2] are generally defined as complex organic bases of plant origin. A few of the more important alkaloids are morphine, cocaine, caffeine, quinine, strychnine, and atropine. They are widely employed as medicinals and are obtained by extraction from the plant source and purified by various precipitations and crystallizations.

Vitamins.[3]—Certain organic compounds have been found to be essential in the diet of man. Absence of these compounds produces scurvy, beriberi, and many other disorders. It is interesting to note that, important as the presence of these substances is in the diet, only very small quantities are needed by man. The supply must be maintained daily either from food or special means. At present, a number of these essential compounds or vitamins have been synthesized, but others are known whose exact chemical structure has not been established. Although vitamins A and D are obtained economically from natural sources (chiefly fish-liver oils), their structures are known. Vitamin C, present in citrus fruits, is manufactured more cheaply by synthetical processes. Vitamin B has been found to consist of a complex mixture of compounds, part of which can be synthesized economically and some of which, with unknown or known chemical structure, are extracted from natural sources.

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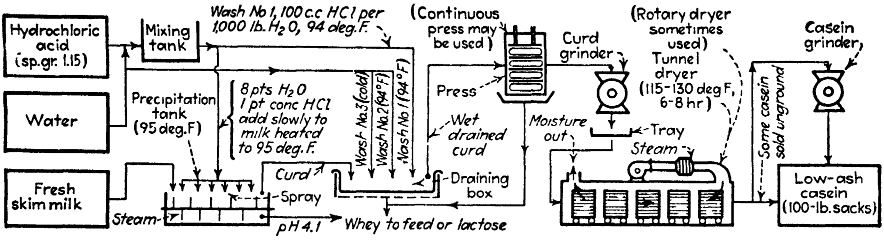
[1] PERRY, *op. cit.*, pp. 1476–1477.

[2] SHONLE, p. 1284, in Rogers Manual, *op. cit.*

[3] SHONLE, p. 1298, *op. cit.;* ROSENBERG, "Chemistry and Physiology of the Vitamins," Interscience Publishers, Inc., New York, 1942.

Chemicals from Milk.—There are available, throughout the United States, some billions of pounds of whey, resulting from the making of cream and of cheese. Much of this whey is wasted each year or used as a cheap animal food. A great deal of study has been given to the exploitation of this raw material and now about 5,000,000 lb. of lactic acid is made annually by fermentation as described in Chap. XXXI. In addition, this country manufactures about 5,000,000 lb. of lactose and 50,000,000 lb. of casein. The lactose has a certain limited consumption, almost entirely in infant foods and pharmaceutical preparations. Casein is a phosphoproteid of high molecular weight (probably near 100,000) with many and varied applications. About three-quarters of the casein now manufactured is consumed as a binder in high-grade coated paper for printing and stationery. Most of the remainder is used in glues, cold-water paints, and plastics. However, the newly developed casein fiber, Aralac, probably consumed over 5,000,000 lb. of casein in 1943.


Hydrochloric acid (sp.gr. 1.15)
Water
Fresh skim milk
Mixing tank
Precipitation tank (95 deg.F)
Steam
Wash No 1, 100 c.c HCl per 1,000 lb. H₂O, 94 deg.F.
8 pts H₂O 1 pt conc HCl add slowly to milk heated to 95 deg. F.
Wash No.3 (cold)
Wash No.2 (94°F)
Wash No 1 (94°F)
Curd
Spray
pH 4.1
Whey to feed or lactose
(Continuous press may be used)
Press
Wet drained curd
Draining box
Curd grinder
Moisture out
Tray
Steam
(Rotary dryer sometimes used)
Tunnel dryer (115-130 deg F, 6-8 hr)
Some casein sold unground
Casein grinder
Low-ash casein (100-lb. sacks)

Note: Alternative methods, all giving casein of different properties, include precipitation with sulfuric or lactic acids (sour whey or allowing milk to sour), or by enzyme action with rennet

Skim milk	3,333 lb.	Water	Variable	Per 100 lb. casein
Hydrochloric acid (sp.gr. 1.15)	19 93 lb.	Electricity	12 Kw.-hr.	
Steam *	1,200 lb.	Direct labor	3 man-hr.	

** Average present practice; can be much reduced*

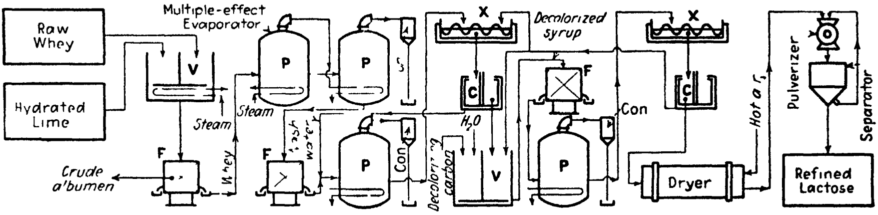
FIG. 7.—Flow sheet for casein—grain-curd process using hydrochloric acid.

Casein[1] is precipitated from skim milk by the use of an acid such as hydrochloric, sulfuric, or lactic acid, or by rennet. The casein resulting from these different methods has somewhat varying properties, and there seems to be more demand for the lactic casein among consumers. This is made by allowing the skim milk to sour naturally or, better, to use a starter fermentation to develop the lactic acid necessary to precipitate the casein. The manufacture through hydrochloric acid is depicted in the flow sheet of Fig. 7 where the casein is carefully precipitated as a grainy curd in a continuous spiral trough reactor, washed, pressed, disintegrated, dried, and pulverized.[1] Whey resulting from this separation seems most suitable for concentration to lactose (Fig. 8) or for fermentation to lactic acid (Fig. 9 of Chap. XXXI).

---

[1] CORWIN, Chap. 44 in Rogers' Manual, *op. cit.*, many references and many data. TRIMBLE and BELL, Methods for Manufacturing Acid Precipitated Casein from Milk, *U.S. Dept. Agr. Circ.* 279, 1938; SUTERMEISTER and BROWNE, "Casein and Its Industrial Applications," Reinhold Publishing Corporation, New York, 1939; ANON., Lactic Acid and Casein from Skim Milk, *Chem. & Met. Eng.*, **43**, 480–483 (1936).

Lactose or milk sugar is much less sweet than sucrose. It has been consumed[2] chiefly in infant feeding. The only commercial source of any importance in the United States is the whey of cheese and casein plant



KEY C, Centrifugal, Con, Condenser, F Filter, P, Vacuum pan; V, Vat, X, Crystallizer

Whey	3000 lb	Steam	4,000 lb	Per 100 lb lactose
$Ca(OH)_2$	7 lb	Electricity	17 kw hr	
Decolorizing carbon	5 lb	Direct labor	1.0 1.5 man hr	
Water	10000 gal			

FIG. 8.—Flow sheet for lactose (milk sugar).

Figure 8 shows the *unit operations* (Op.) and *unit processes* (Pr.) involved in the manufacture of lactose.

The raw whey is mixed with hydrated lime in a vat heated with steam coils (Pr.).

The precipitated albumin is removed by filtration (Op.).

The mother liquor, containing the lactose, is evaporated in multiple-effect vacuum evaporators (Op.).

The concentrated sirup is filtered to remove any foreign matter and concentrated further in a vacuum pan (Op.).

The sirup from this evaporator is crystallized and centrifuged. The mother liquor is sent back to the vacuum pan to be further concentrated to obtain another crop of lactose crystals. The mother liquor from this second crop of crystals is concentrated and sold as a by-product for its riboflavin content (Op.).

The crude lactose crystals are treated with water and activated carbon to remove coloring impurities (Op.).

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[1] Fuller details of this process are given by a pictured flow sheet, *Chem. & Met. Eng.*, **47**, 427 (1940); TRIMBLE and BELL, *op. cit.*, p. 25; CHRISMAN, Success in By-Production Demands Quality Control, *Food Industries*, **12**, 45 (1940).

[2] HORNE, Sugar Industries of the United States, *Ind. Eng. Chem.*, **27**, 989 (1935).

Filtration removes the carbon and the decolorized sirup is concentrated, crystallized, and centrifuged (Op.).

The mother liquor is returned to the vat containing the decolorizing carbon and the crystals are dried, pulverized, and made ready for the market (Op.).

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